Electronic Supplementary Information

Green Chemistry

An environmentally benign, mild, and catalyst-free reaction of quinones with heterocyclic ketene aminals in ethanol: site-selective synthesis of rarely fused [1,2-*a*]indolone derivatives *via* an unexpected anti-Nenitzescu strategy†

Bei Zhou,[‡a] Zhi-Cheng Liu,[‡a,b] Wen-Wen Qu,[b] Rui Yang,[b] Xin-Rong Lin,[a] Sheng-Jiao Yan,*[a] and Jun Lin*[a]

[a]*Key Laboratory of Medicinal Chemistry for Natural Resource (Yunnan University), Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming, 650091, P. R. China.*
[b]*Department of Applied Chemistry, Faculty of Science, Kunming University of Science and Technology, Kunming, 650500, P. R. China.*
[‡]These authors contributed equally to this paper.

**E-mail: yansj@ynu.edu.cn, linjun@ynu.edu.cn*

Tel & Fax: +86 871 65033215

Table of Contents

I ^{1}H NMR and ^{13}C NMR Spectra of Compounds 3

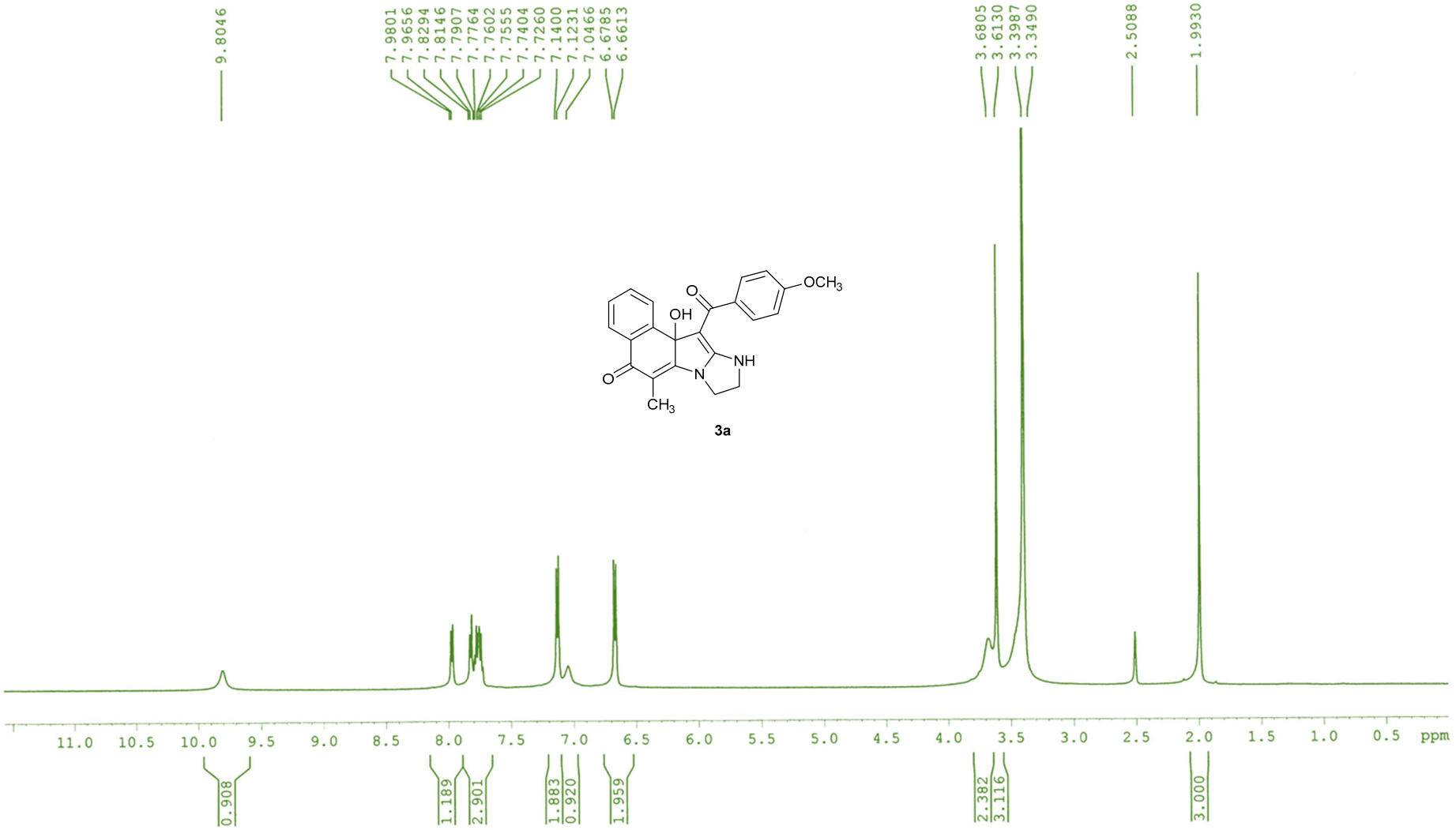


Fig. S1 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3a**

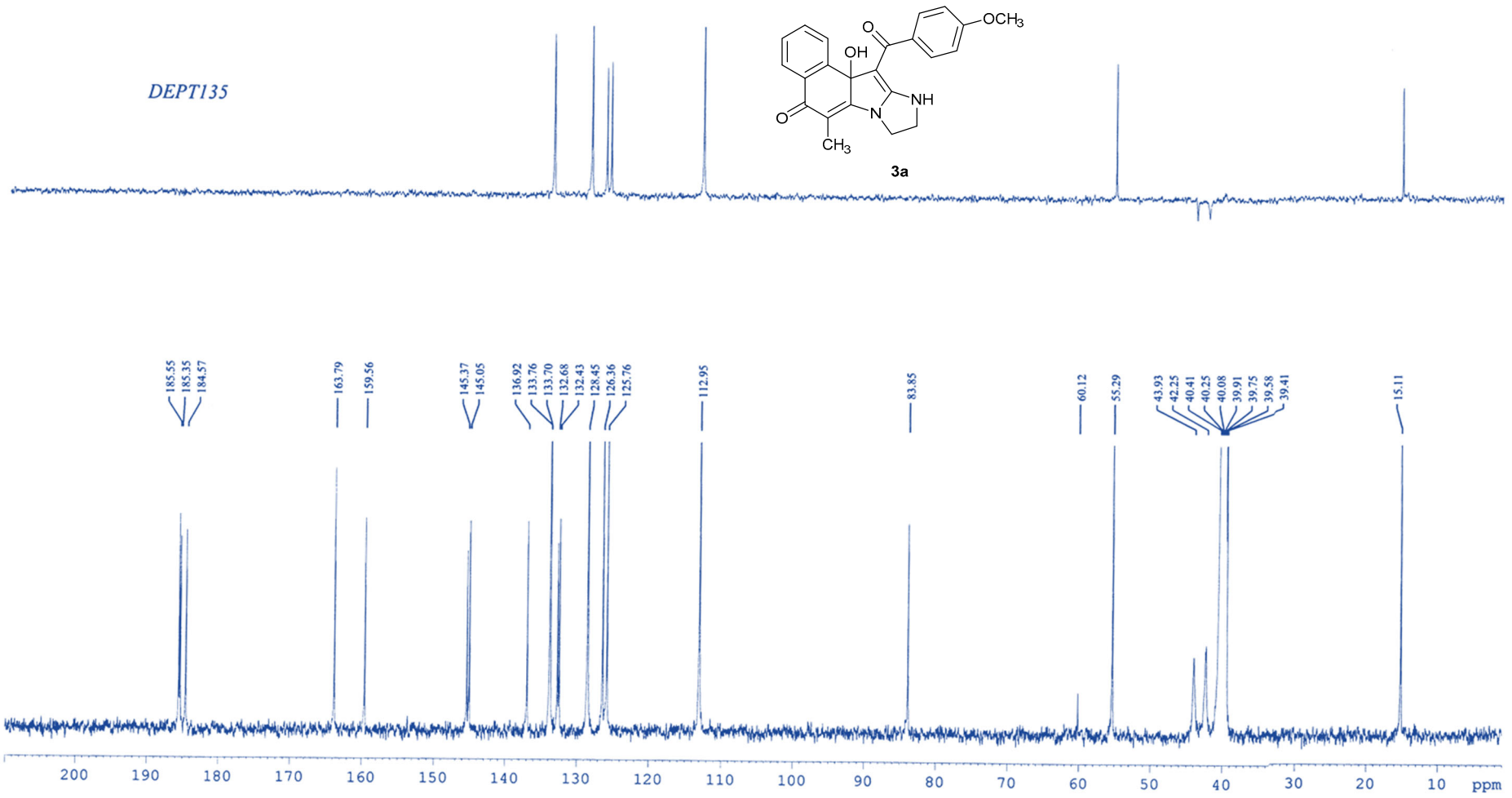


Fig. S2 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3a**

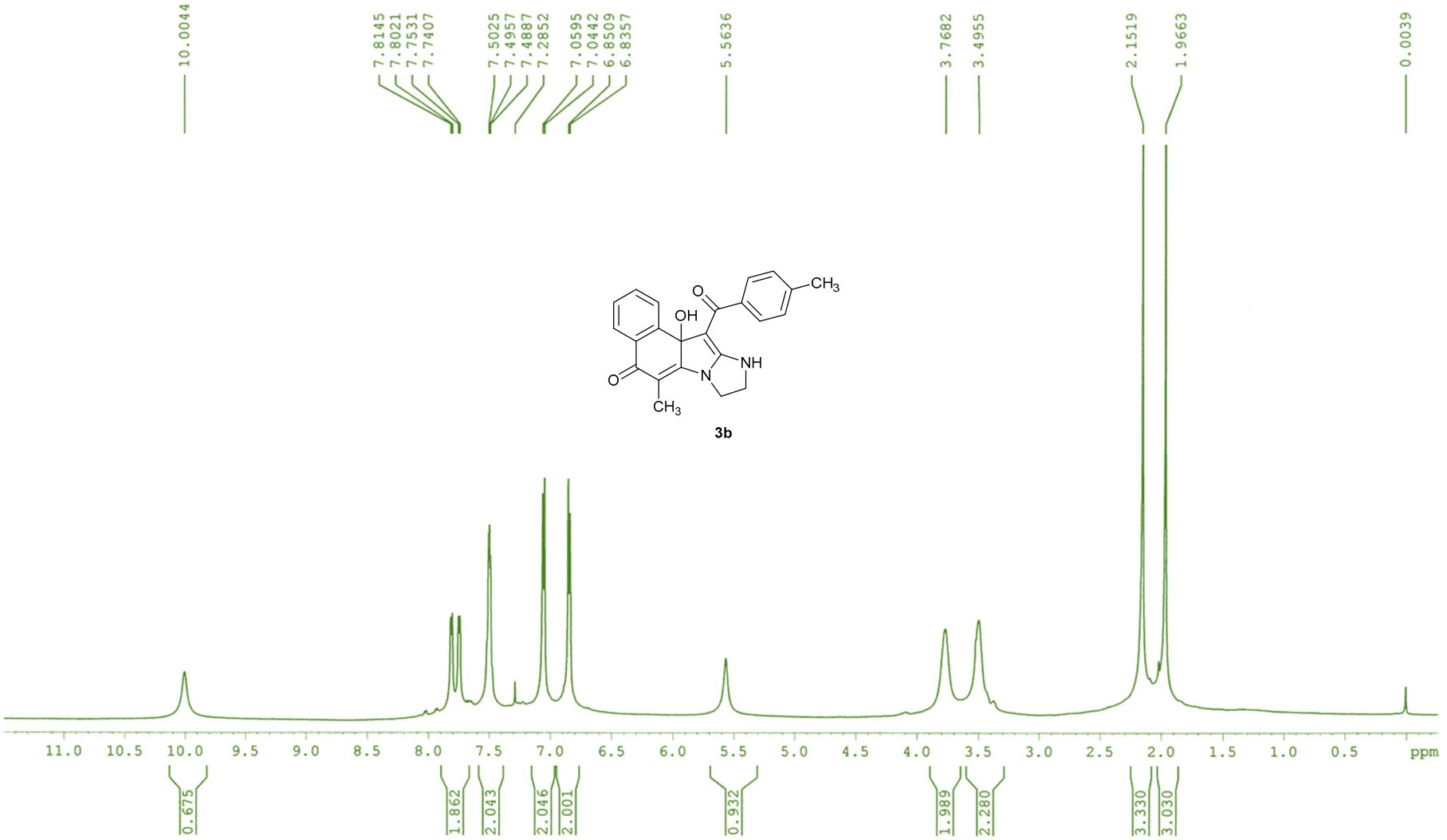


Fig. S3 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3b**

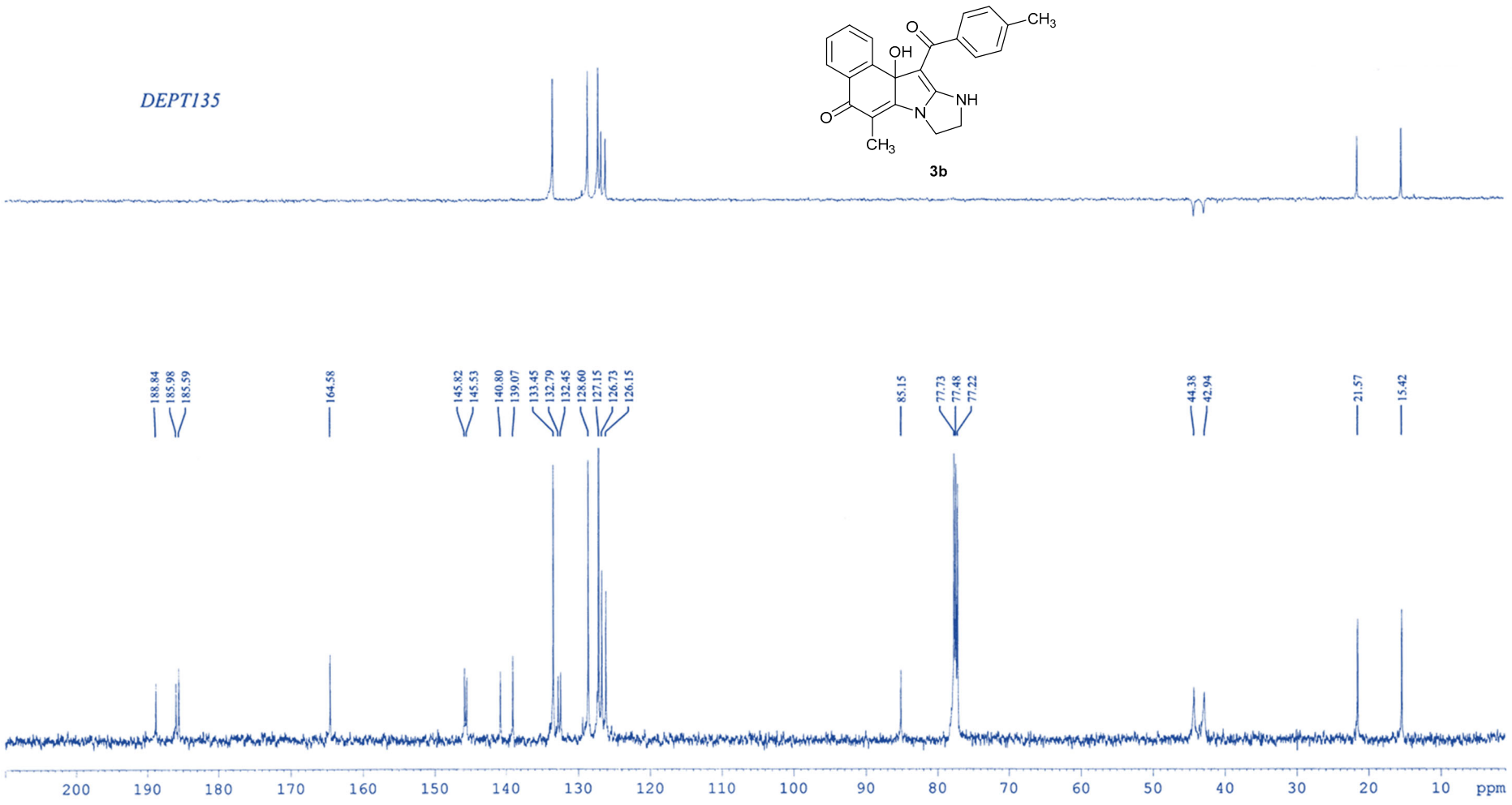


Fig. S4 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3b**

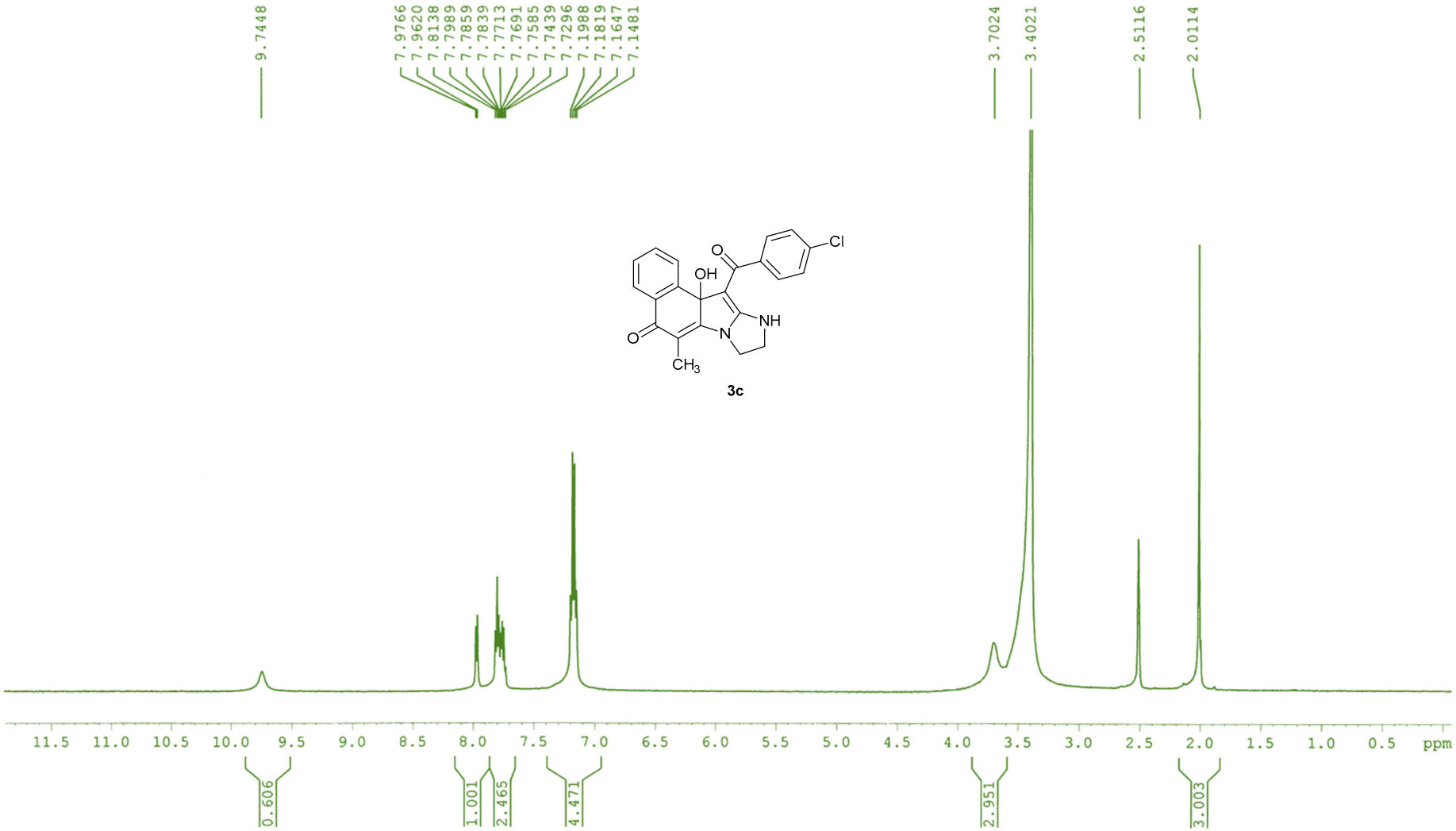


Fig. S5 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3c**

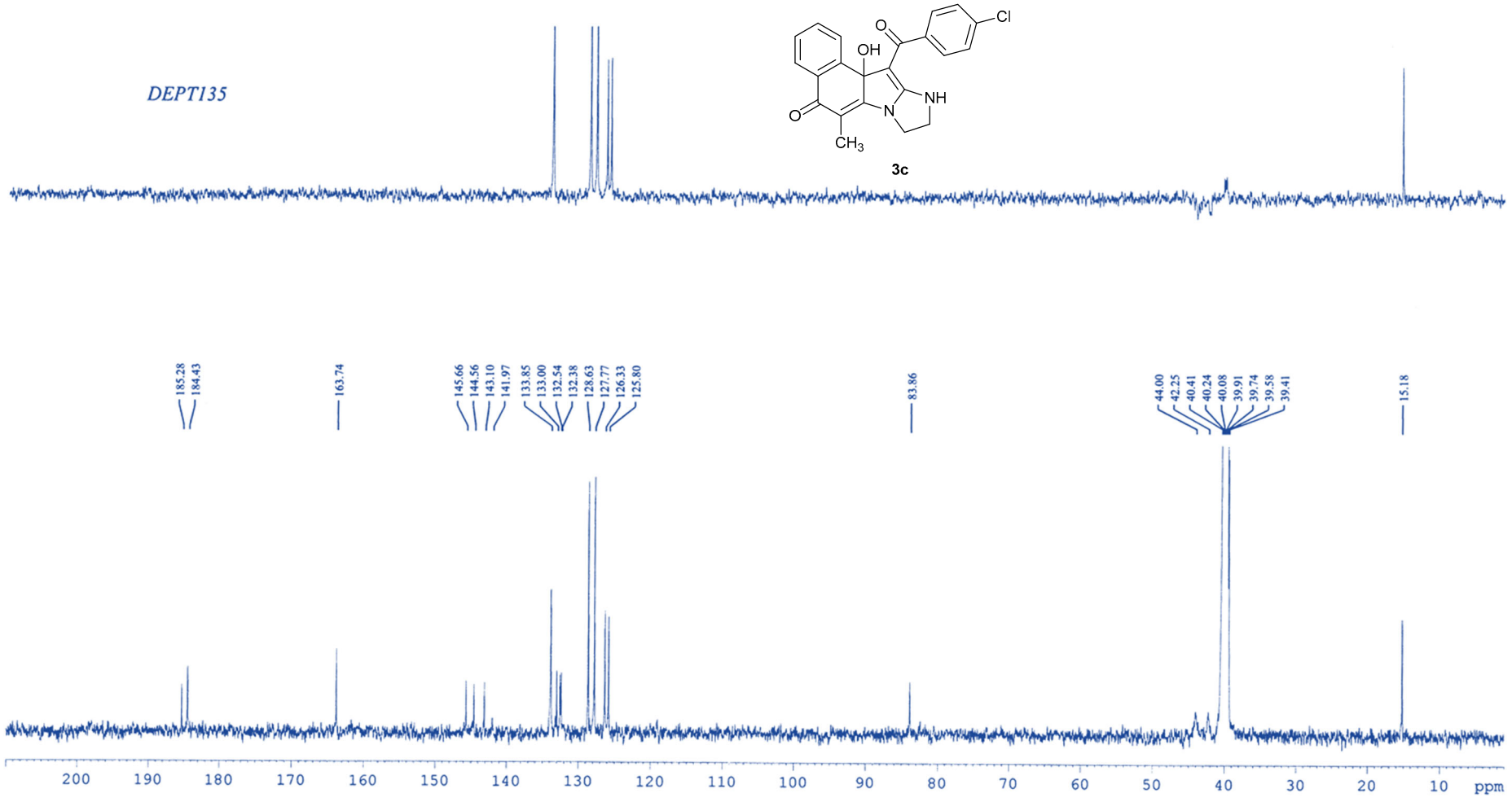


Fig. S6 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3c**

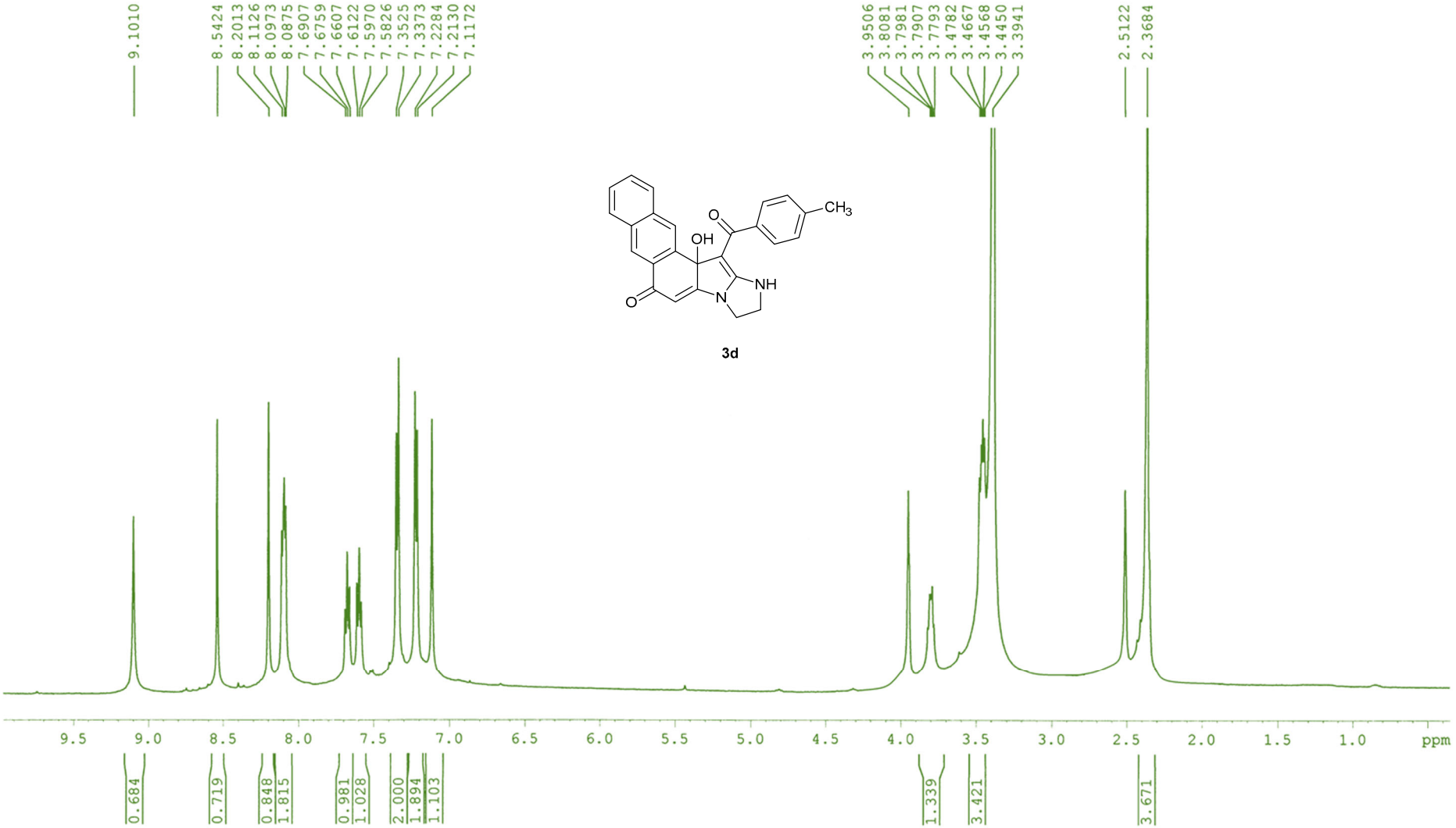


Fig. S7 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3d**

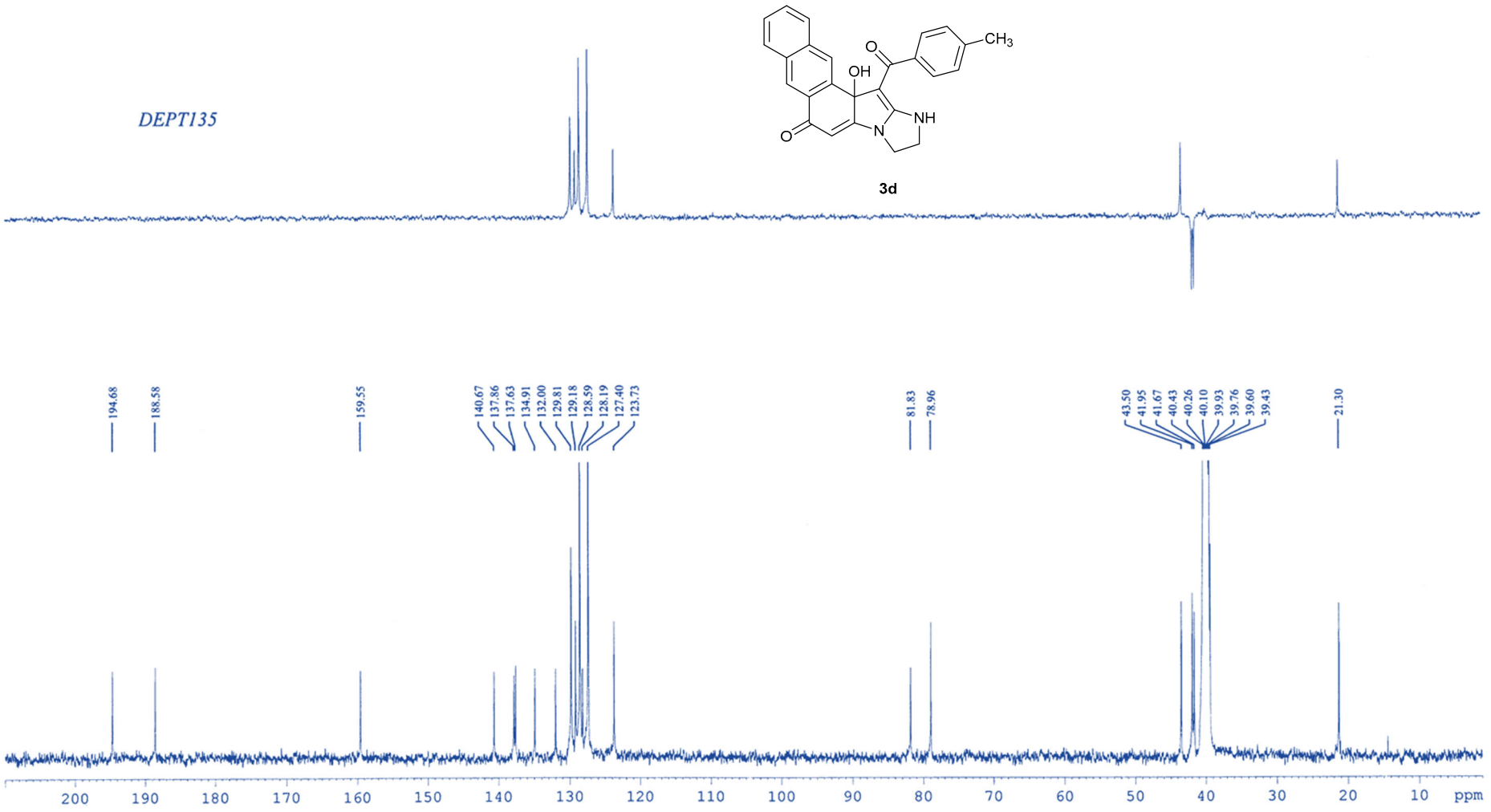


Fig. S8 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3d**

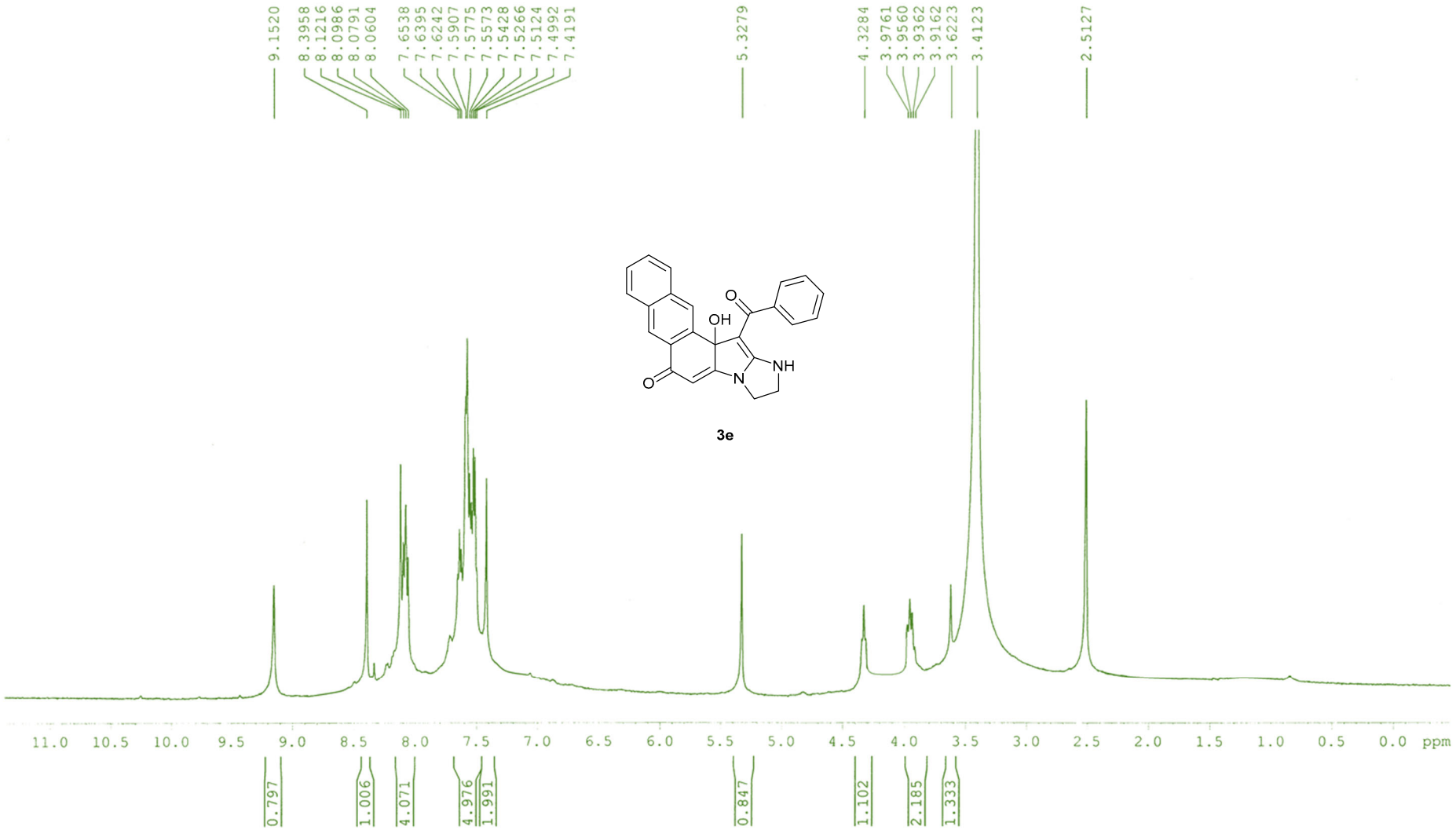


Fig. S9 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3e**

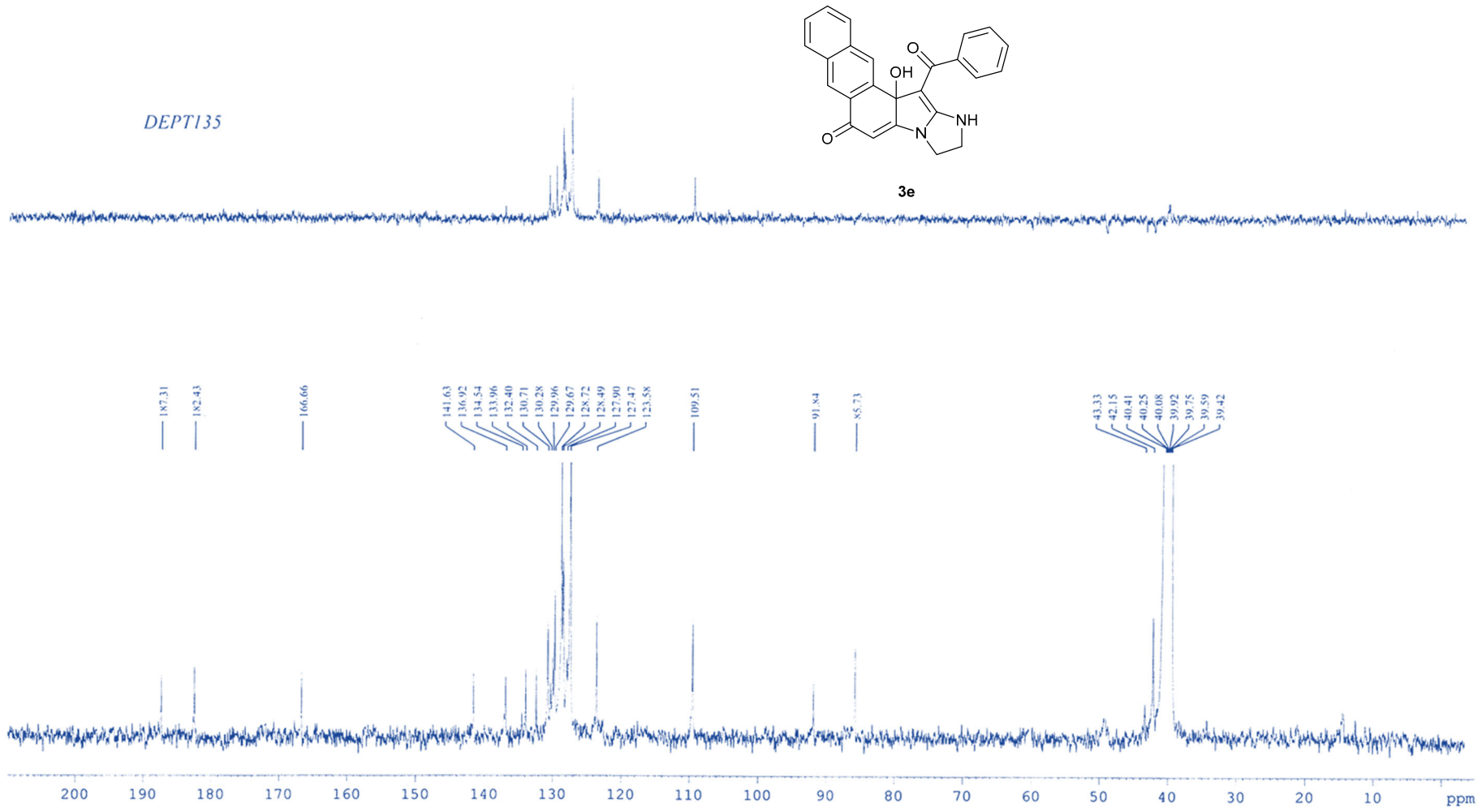


Fig. S10 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3e**

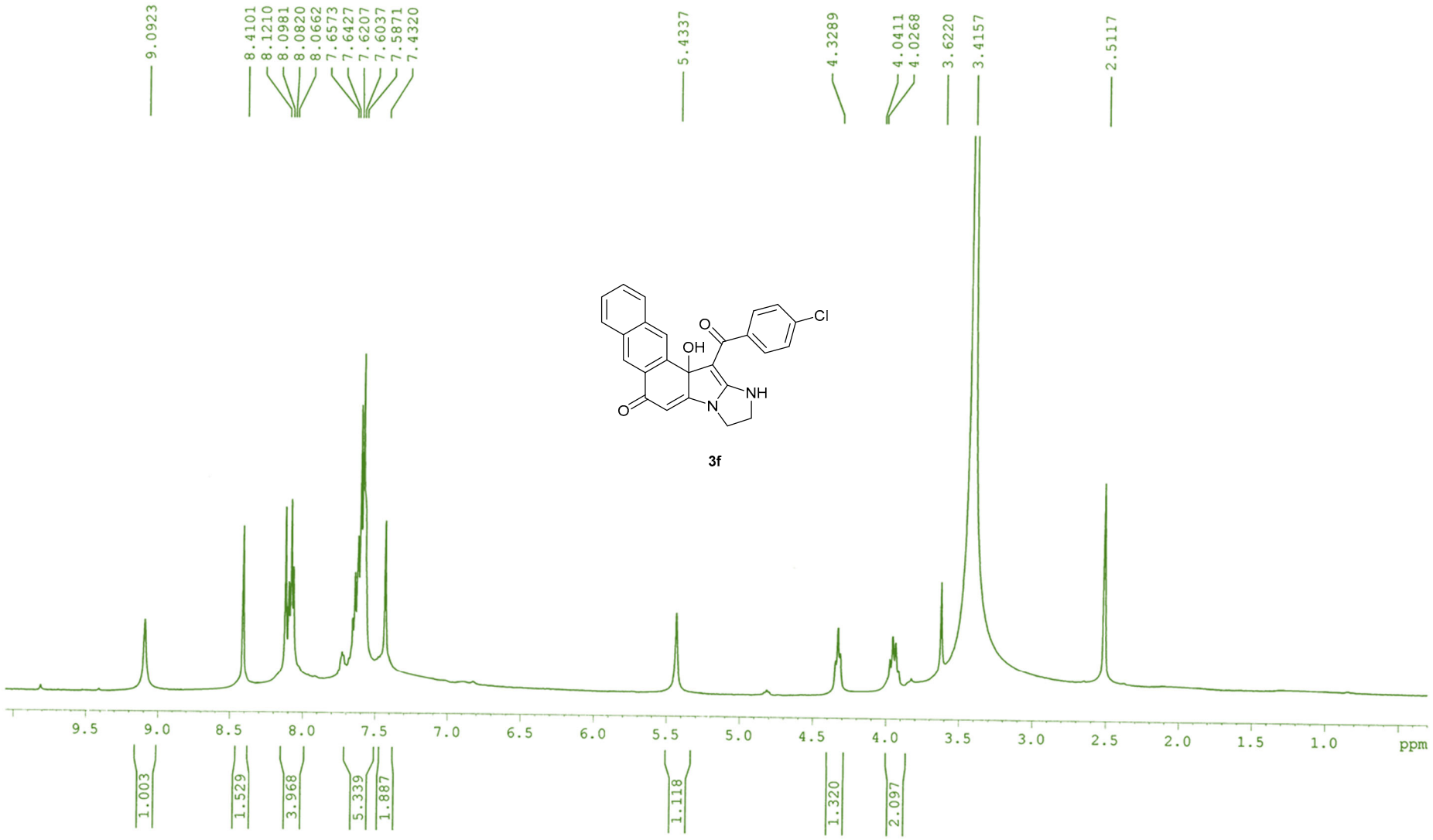


Fig. S11 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3f**

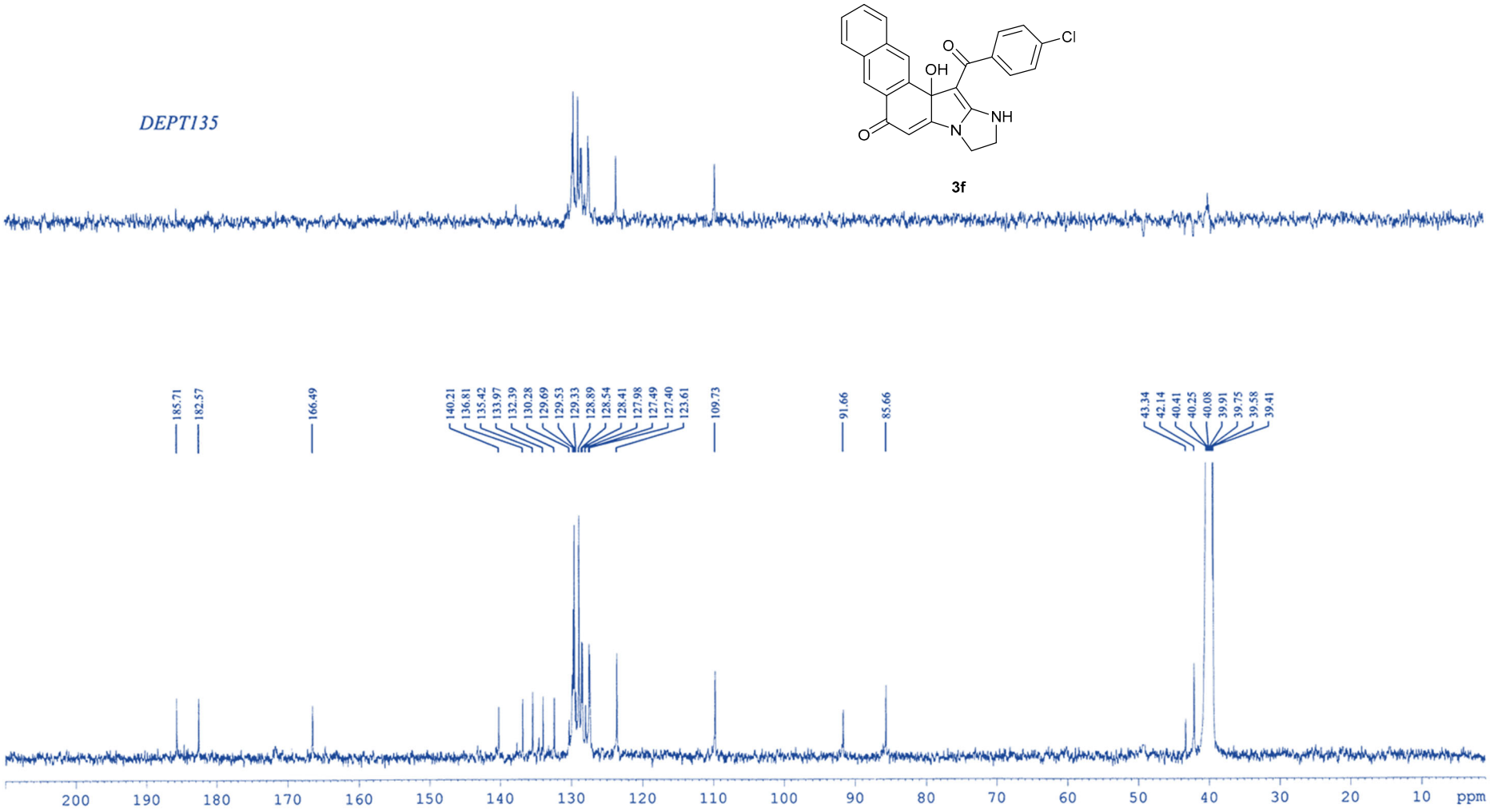


Fig. S12 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3f**

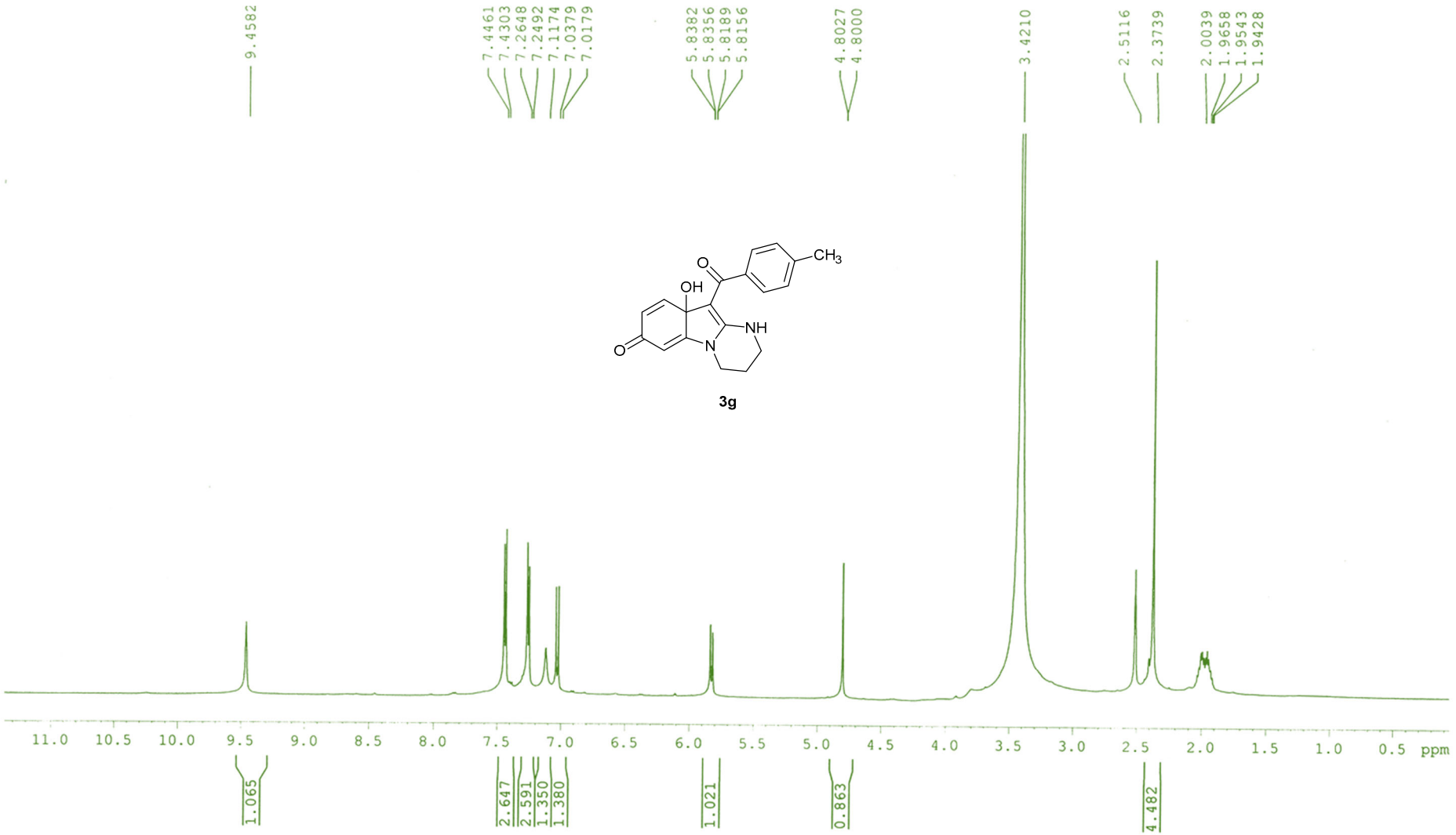


Fig. S13 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3g**

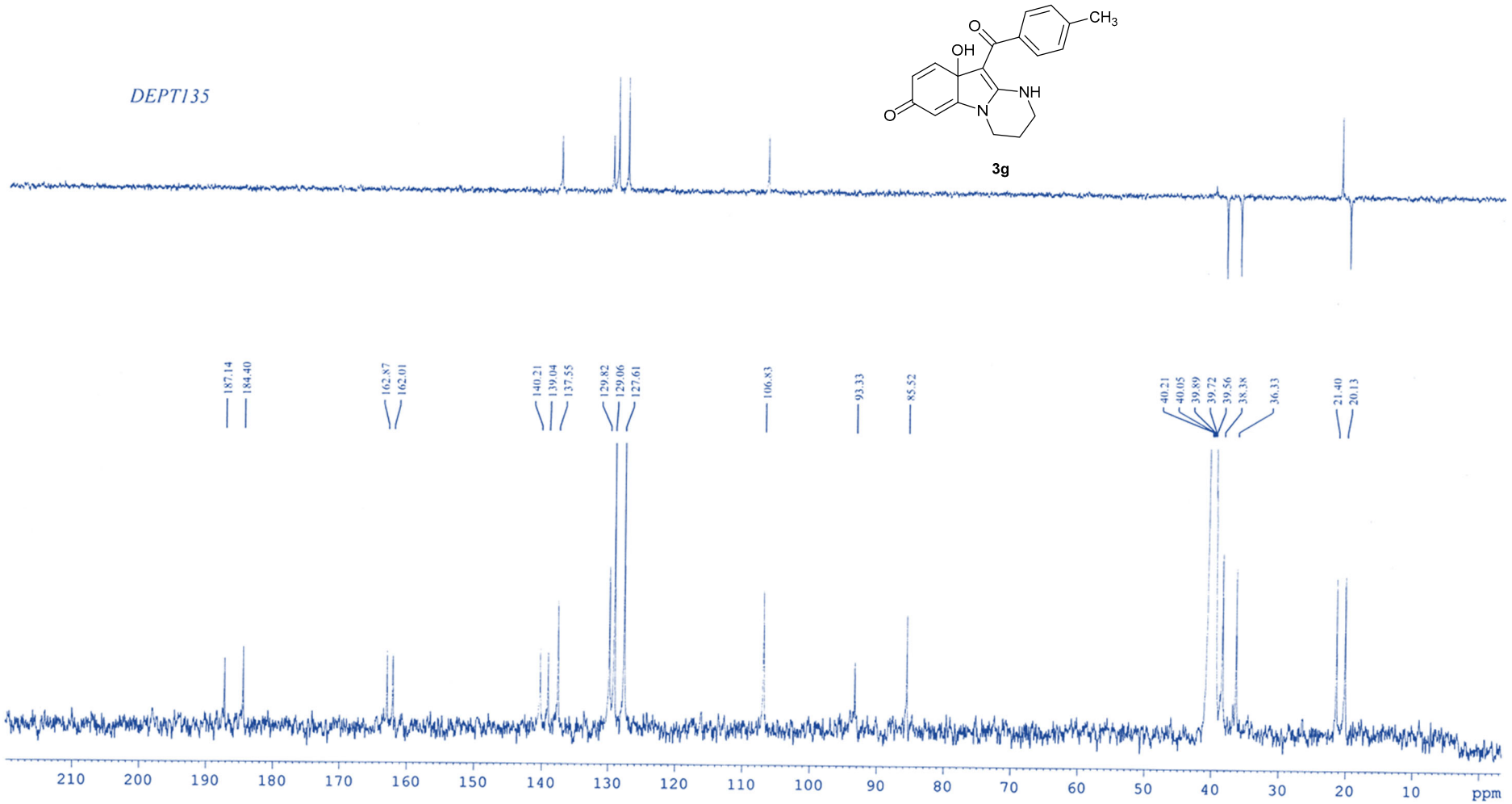


Fig. S14 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3g**

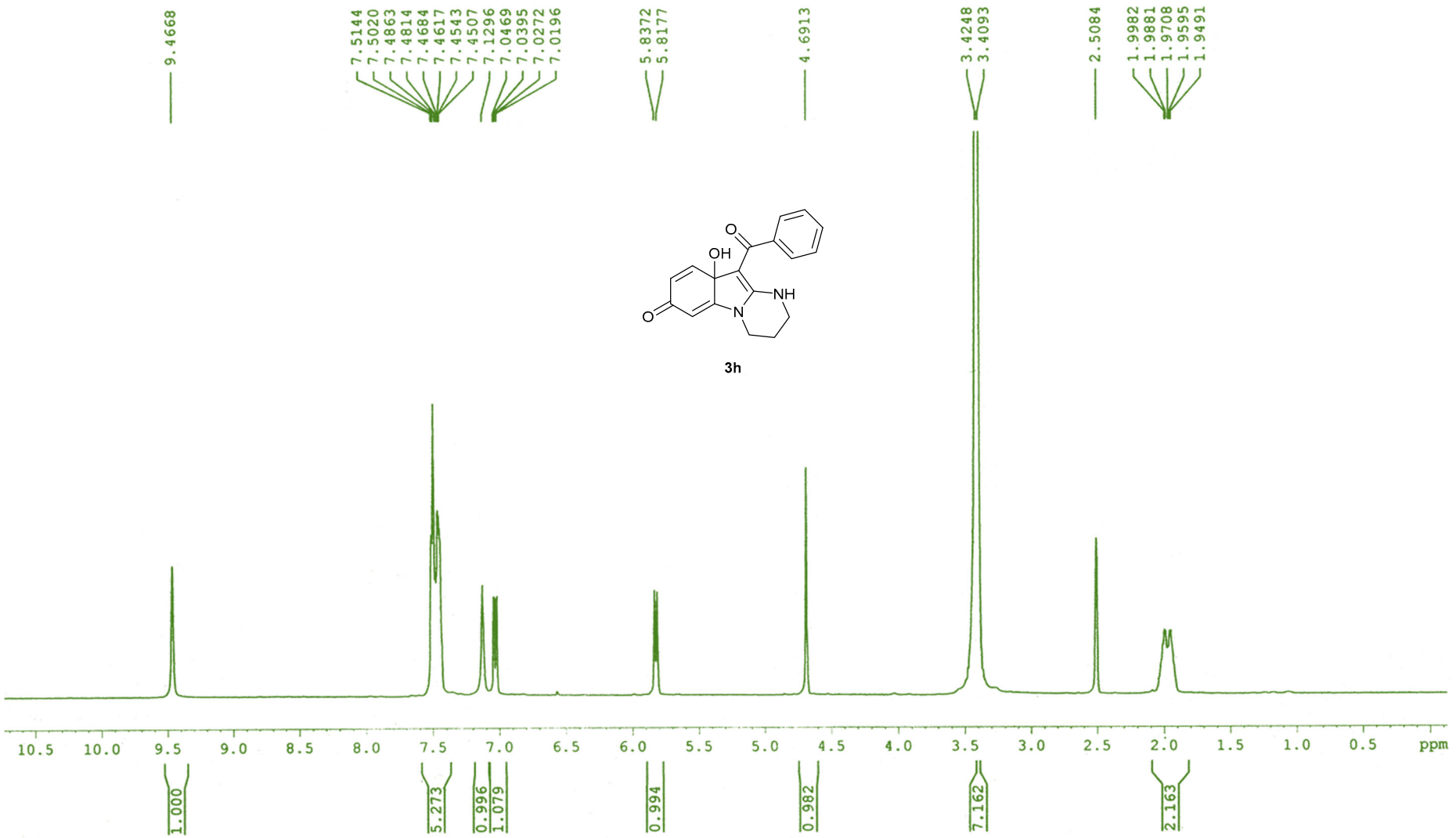


Fig. S15 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3h**

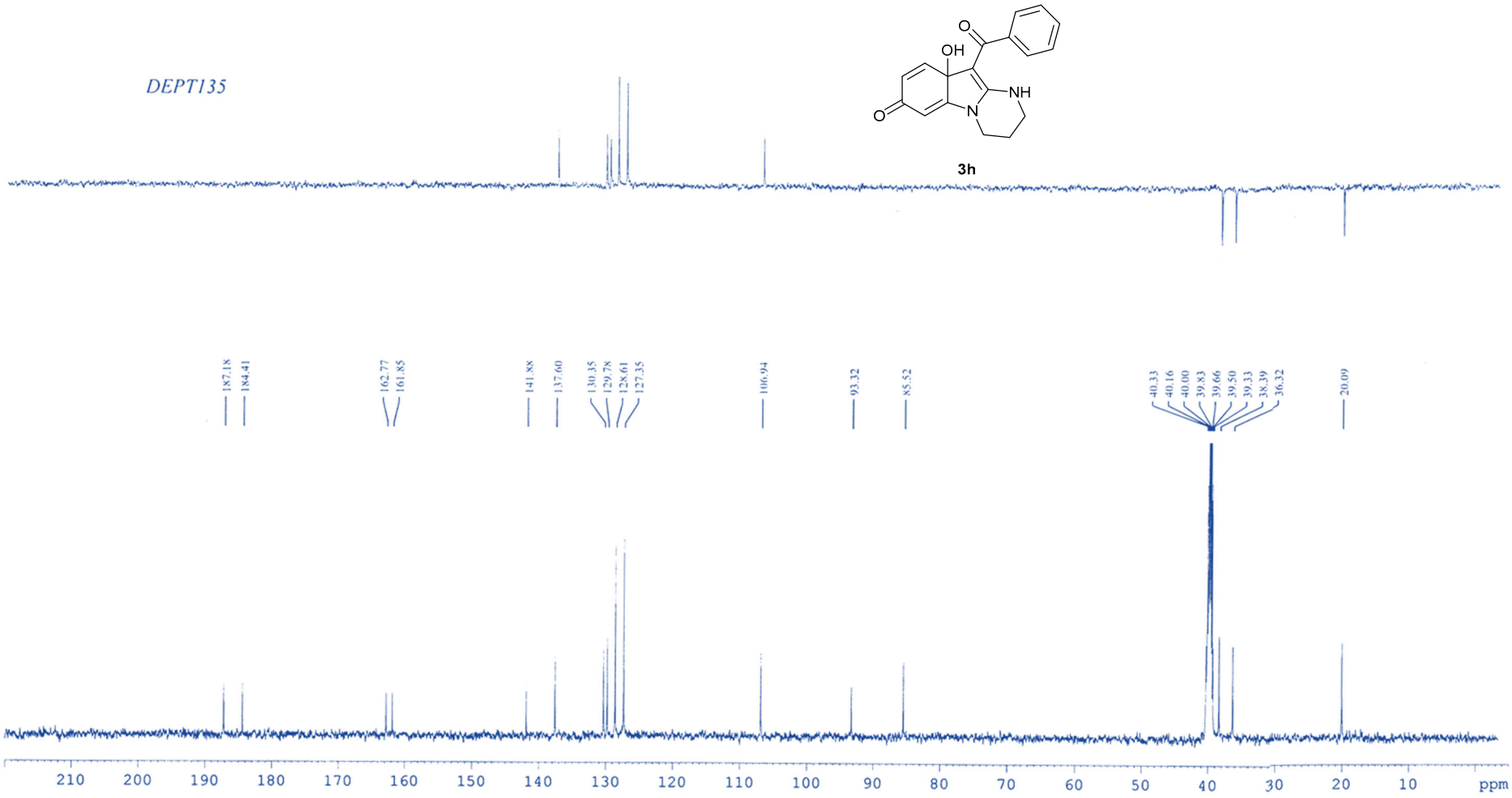


Fig. S16 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3h**

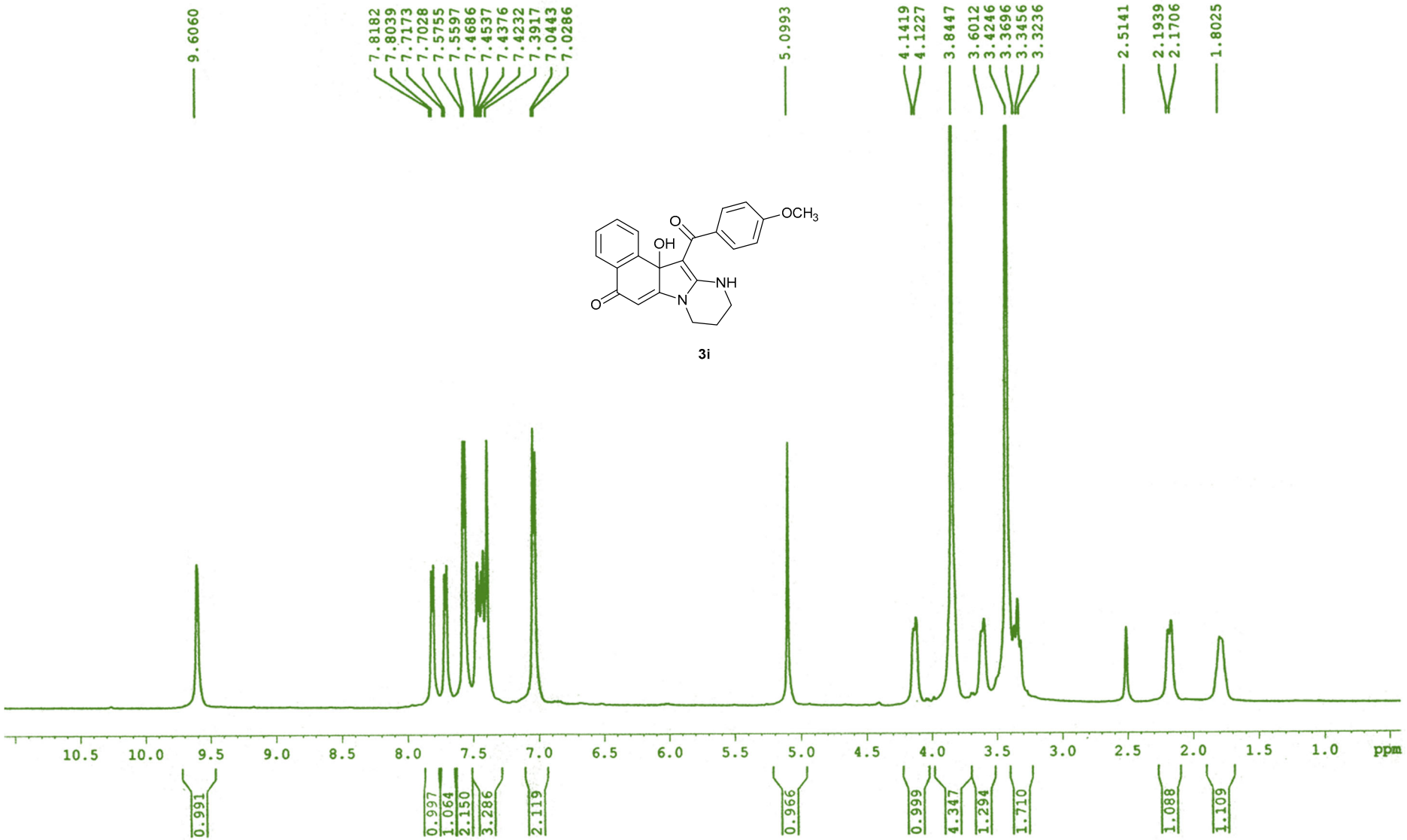


Fig. S17 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3i**

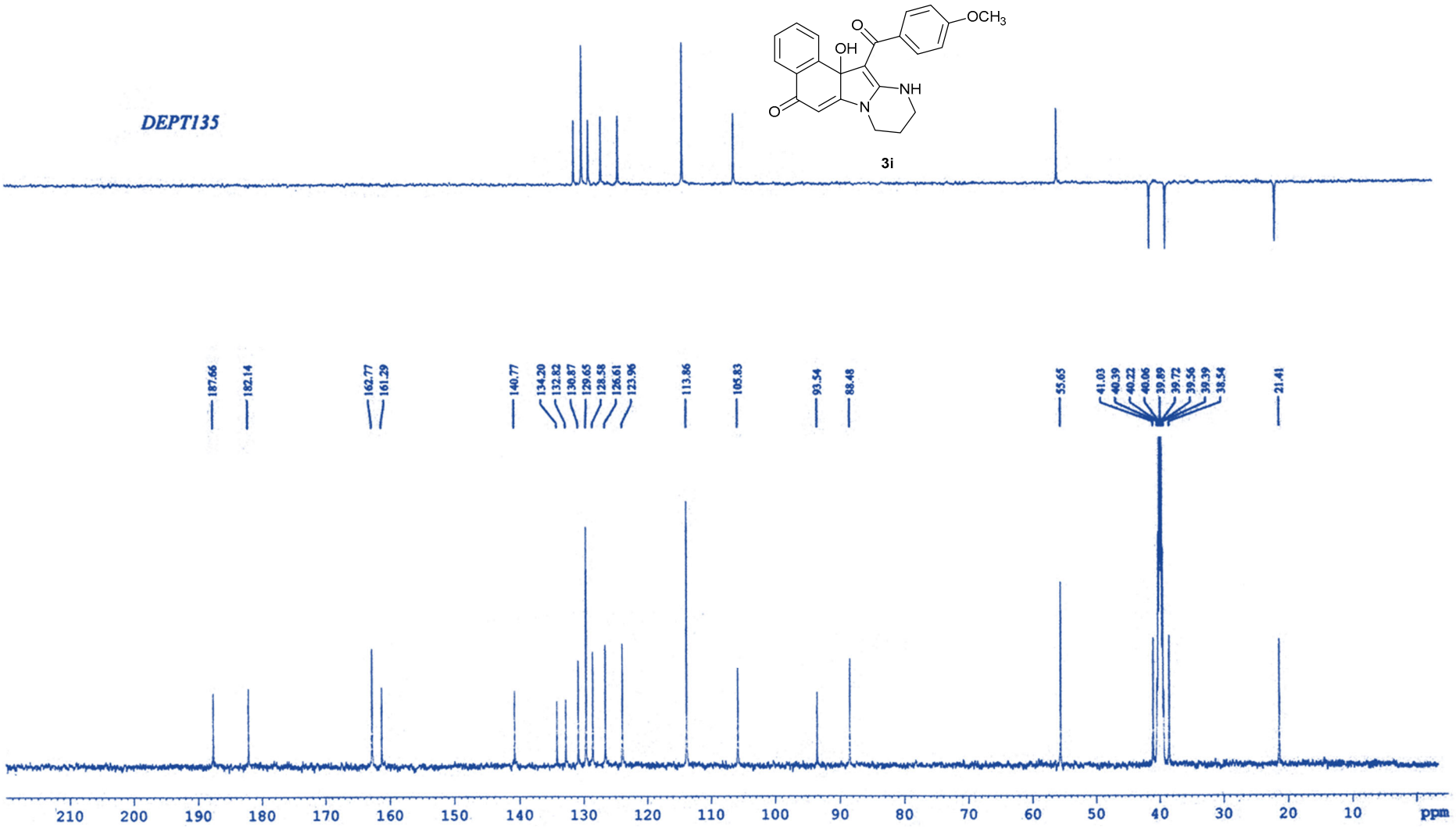


Fig. S18 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3i**

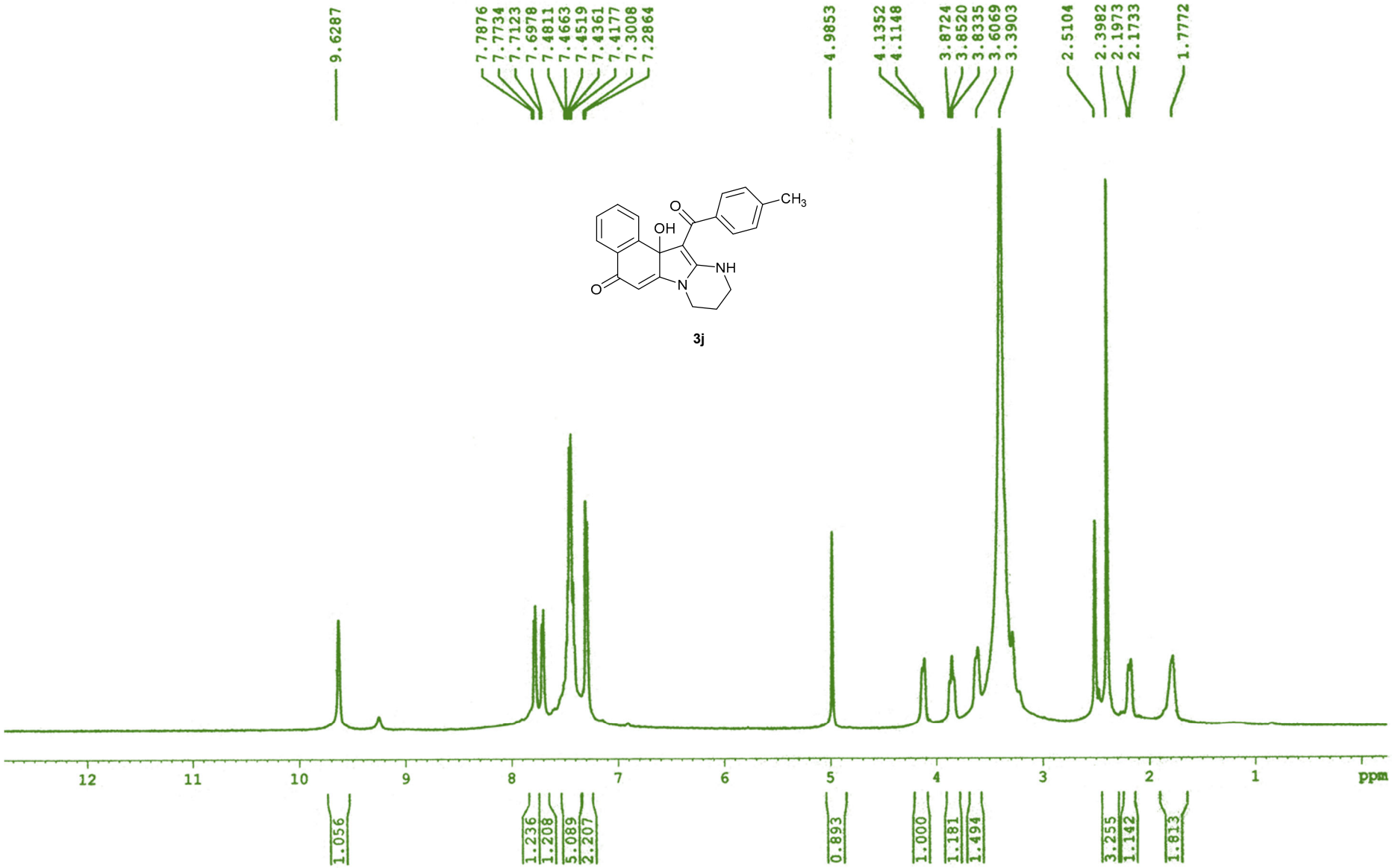


Fig. S19 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3j**

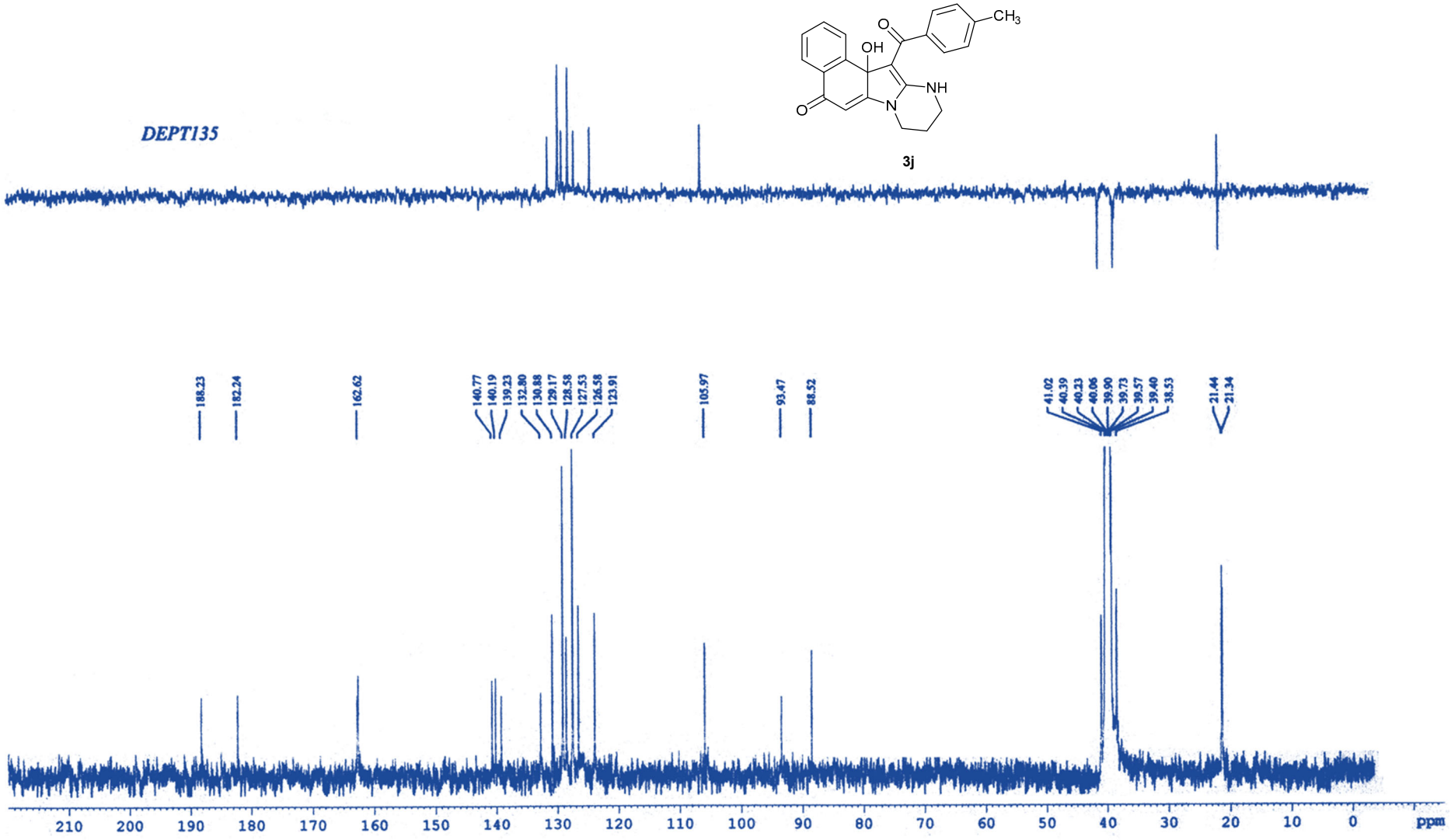


Fig. S20 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3j**

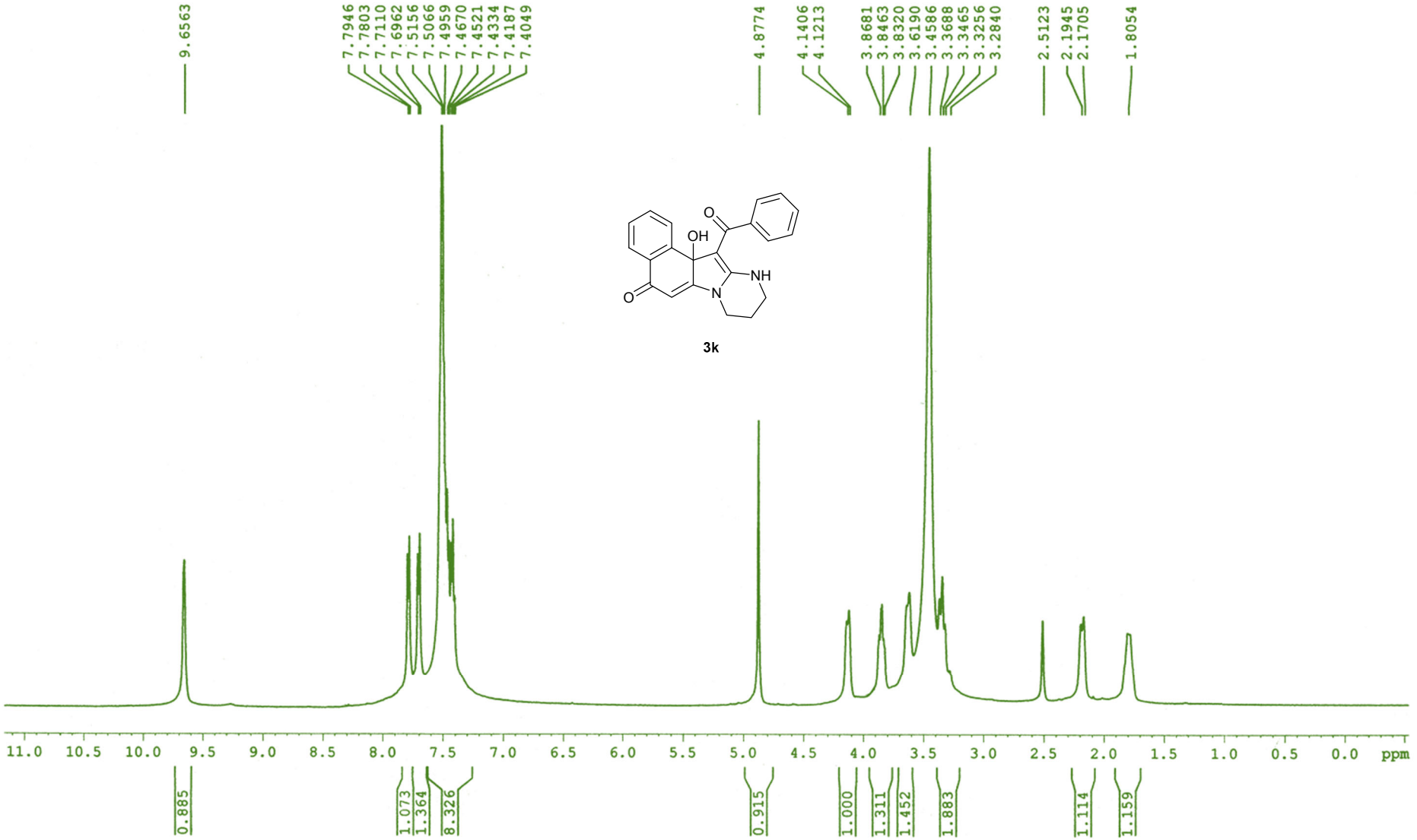


Fig. S21 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3k**

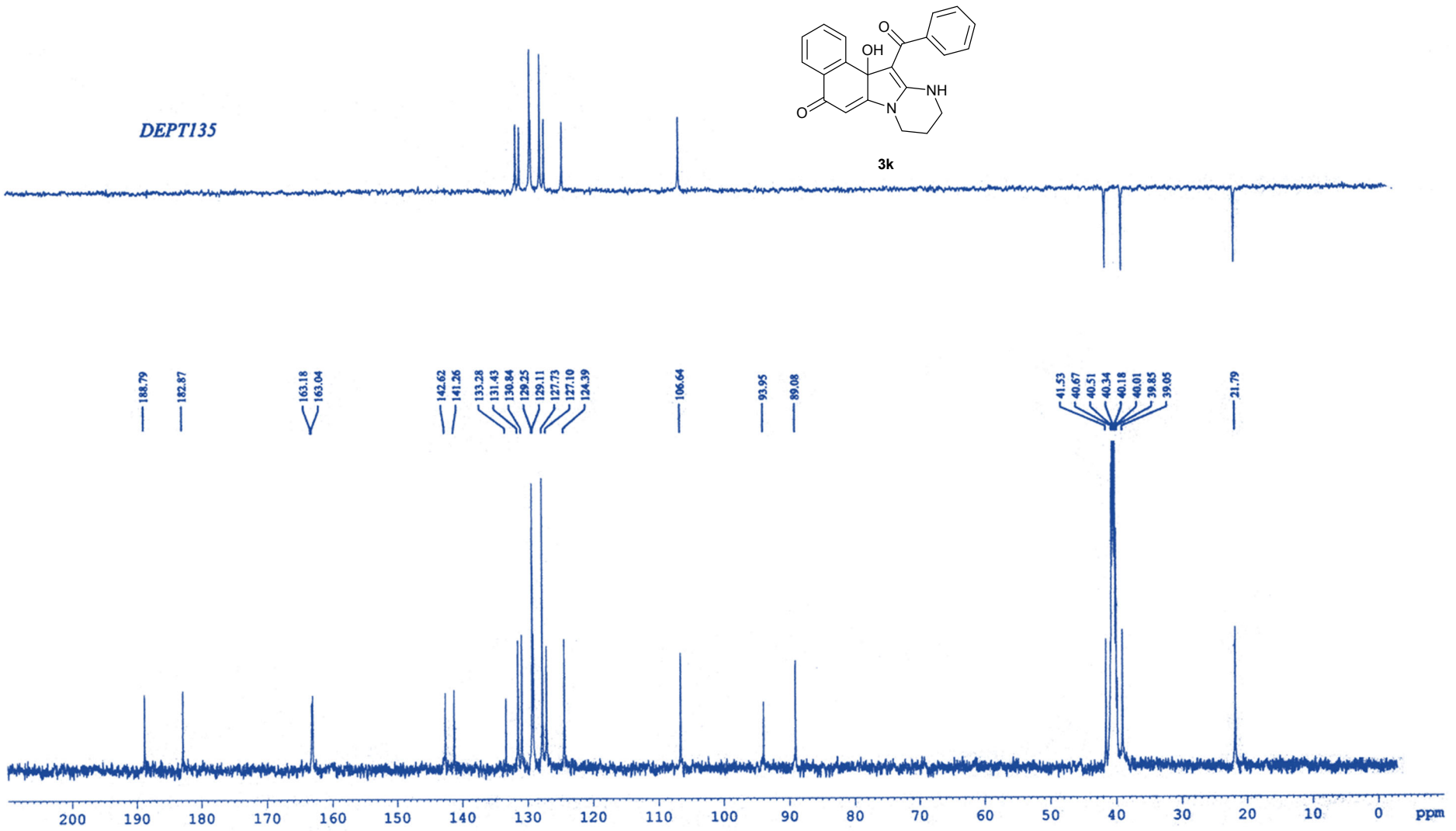


Fig. S22 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3k**

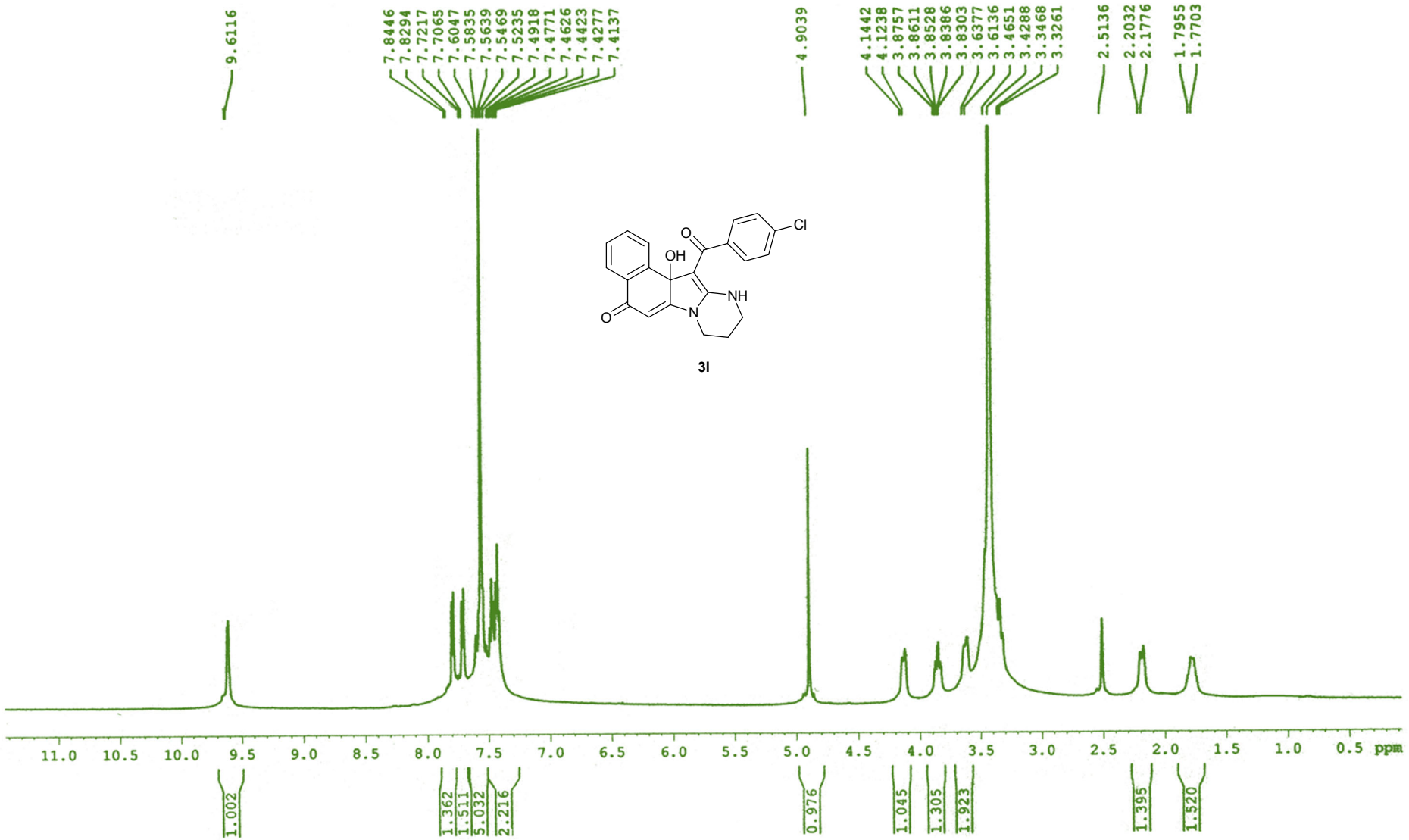


Fig. S23 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3l**

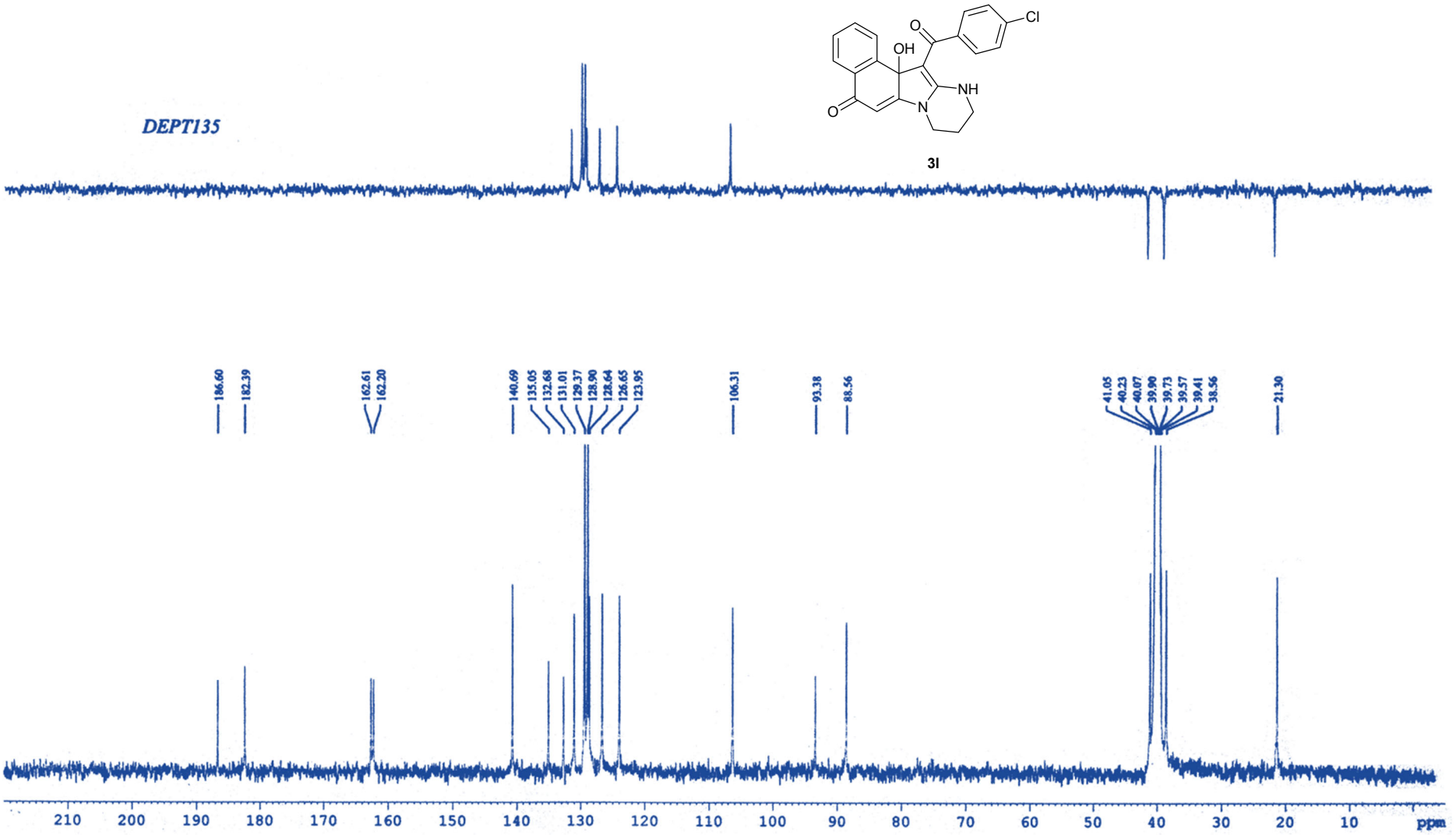


Fig. S24 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3l**

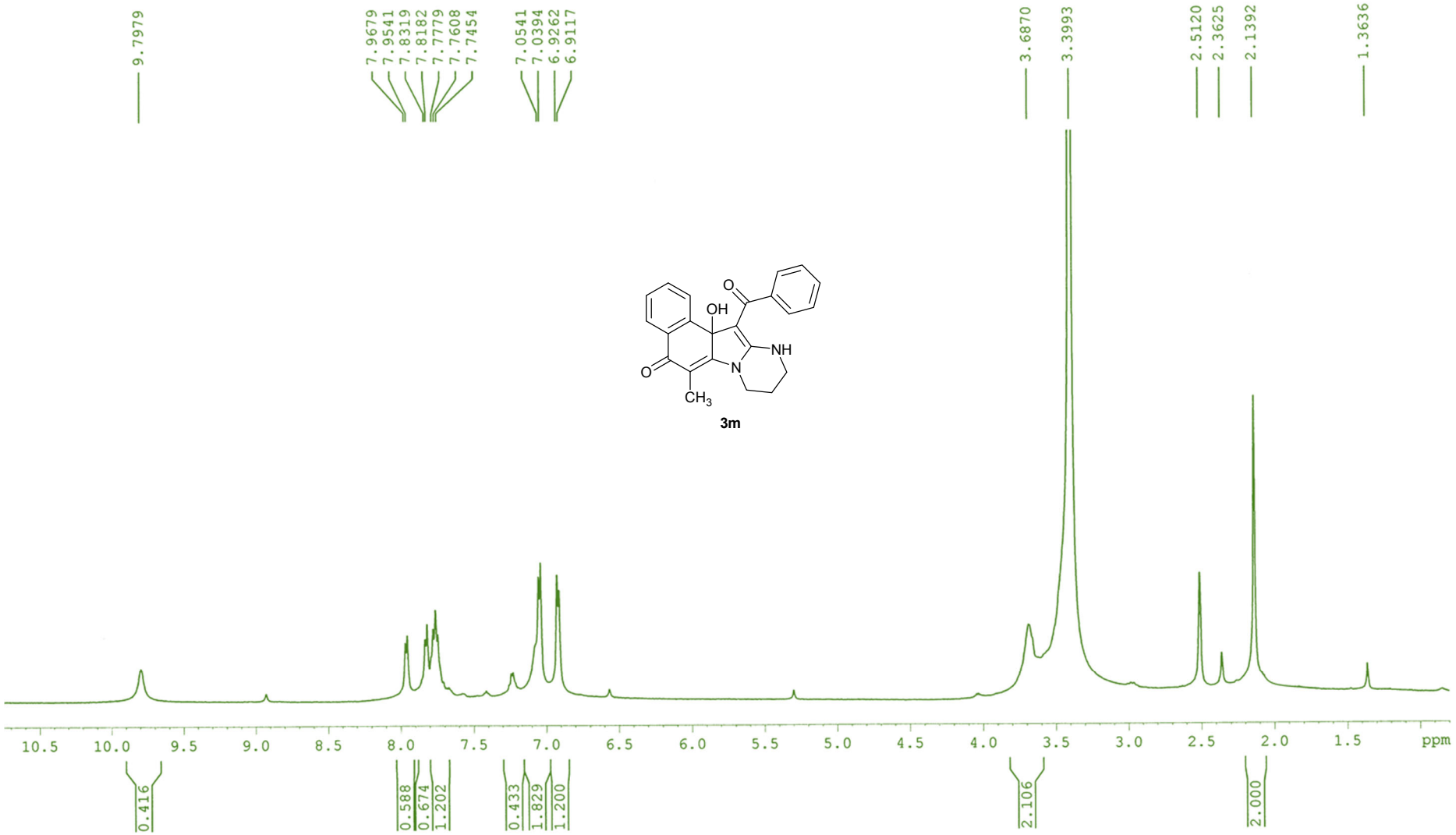


Fig. S25 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3m**

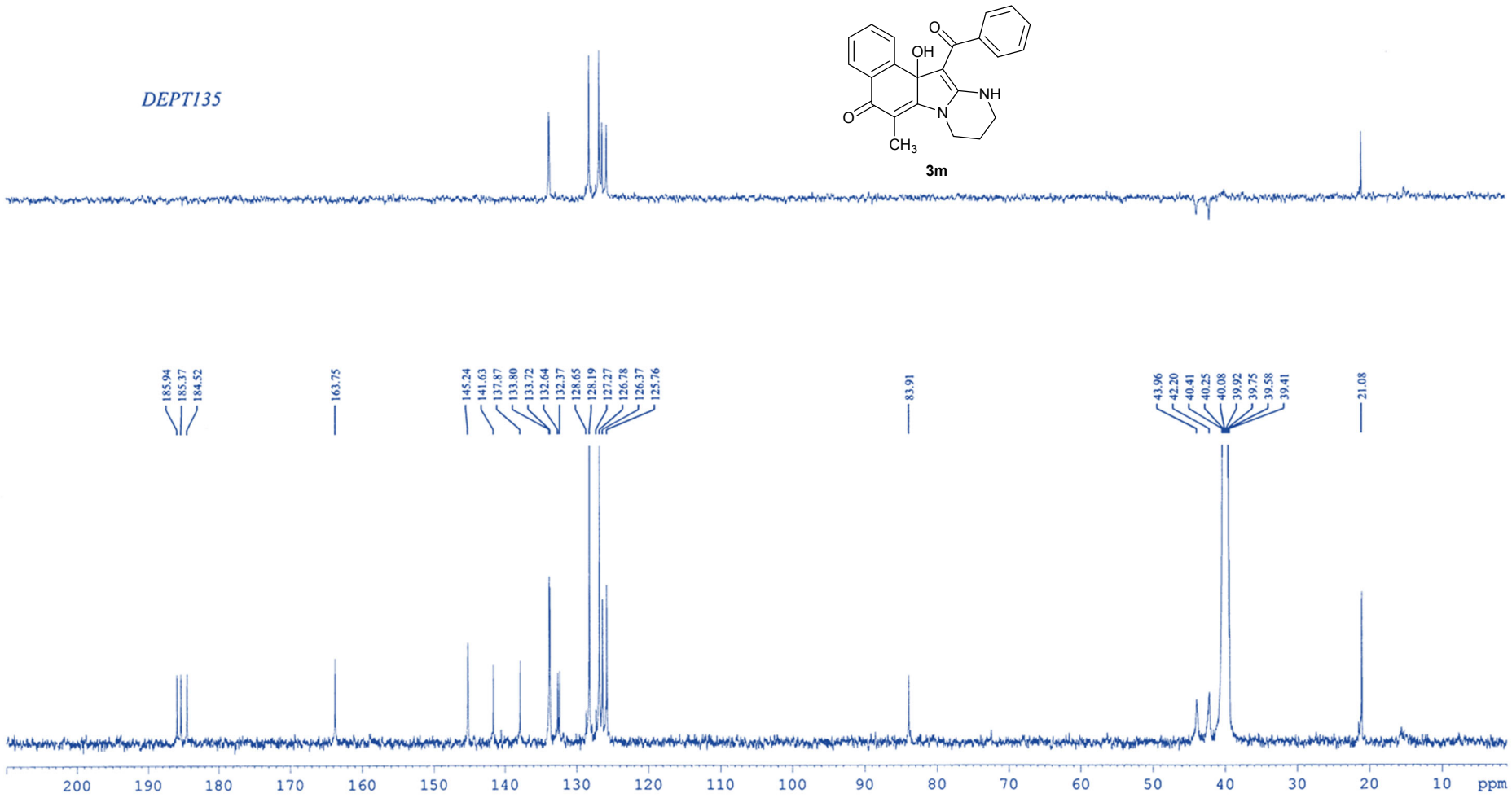


Fig. S26 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3m**

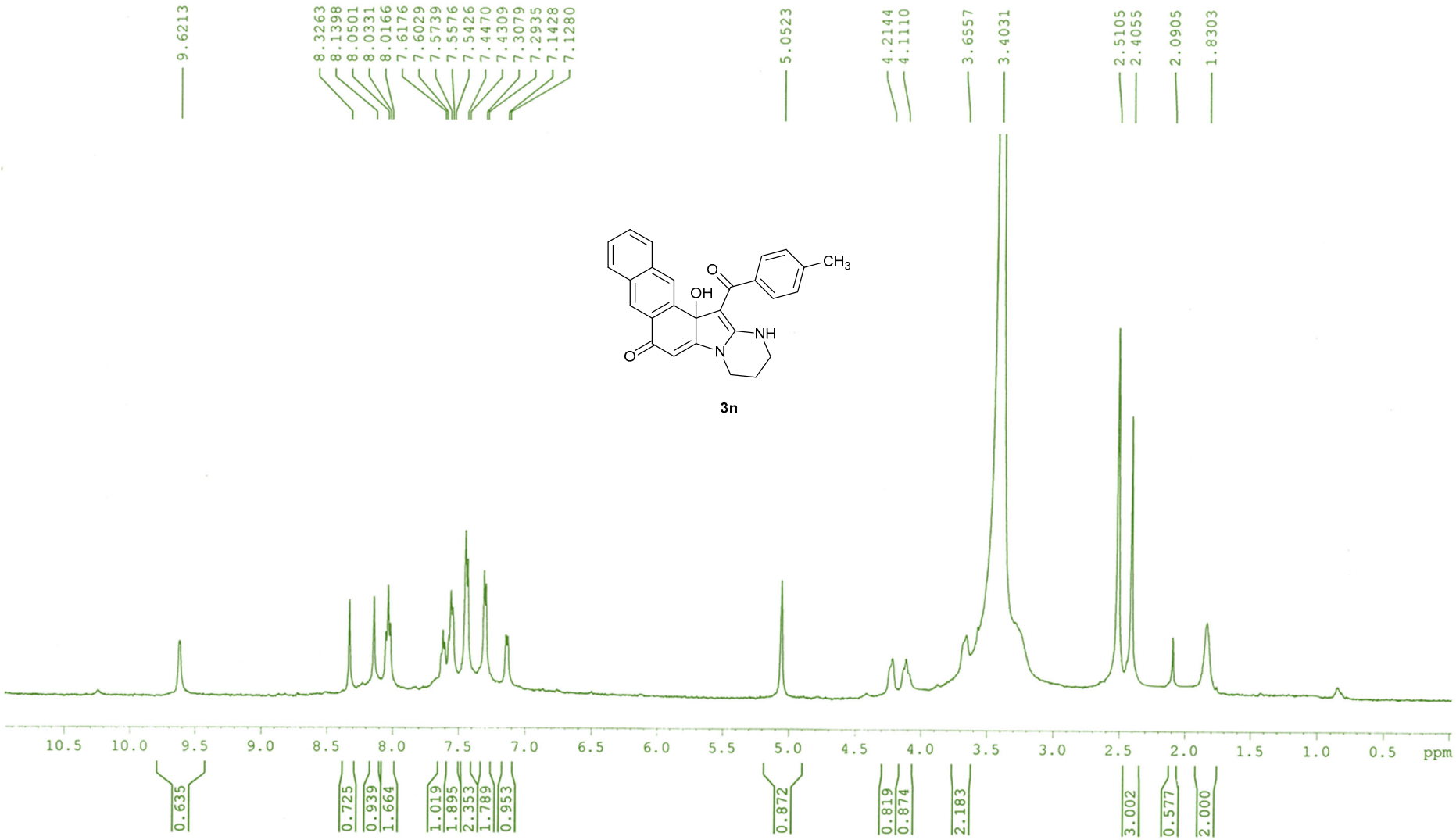


Fig. S27 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3n**

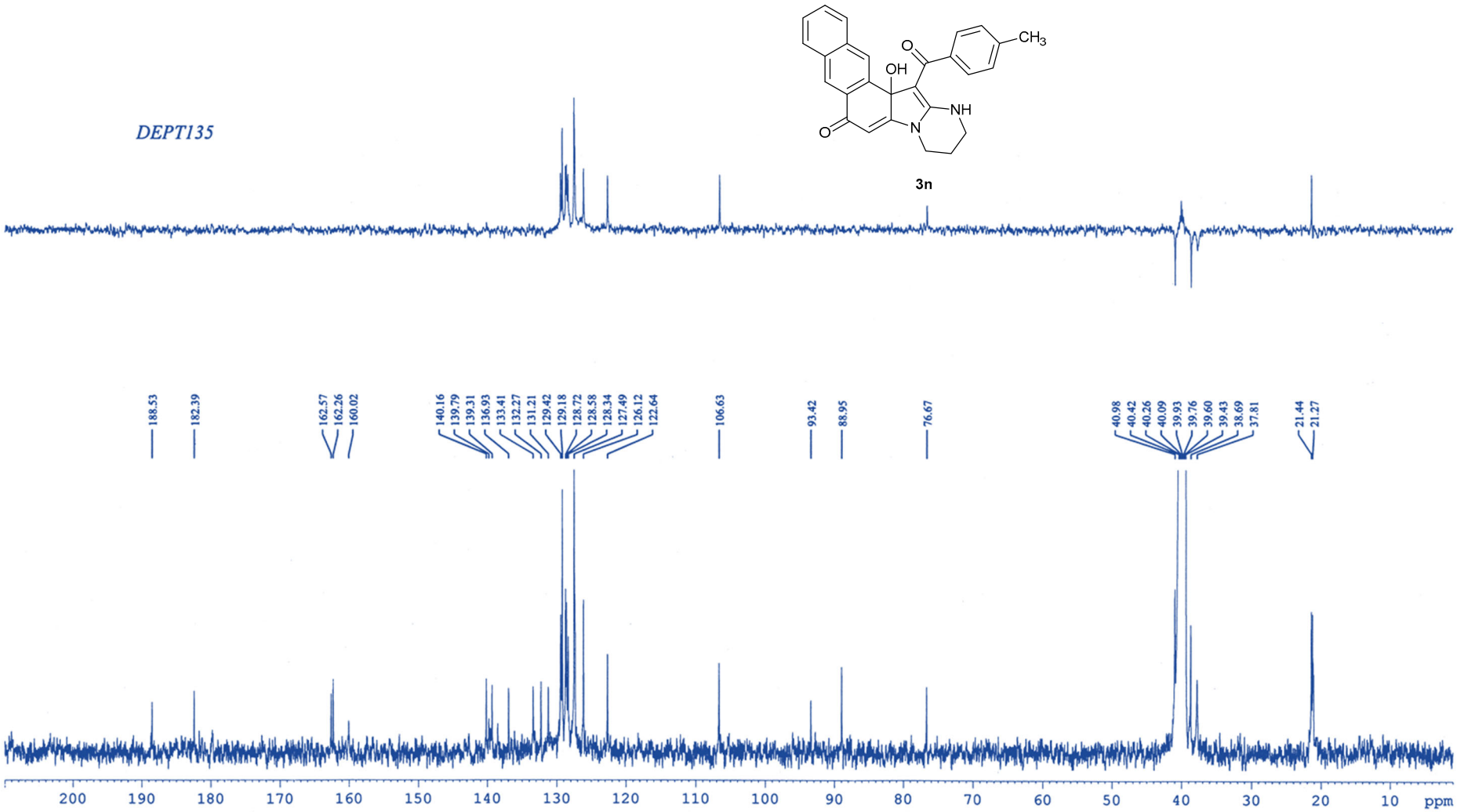


Fig. S28 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3n**

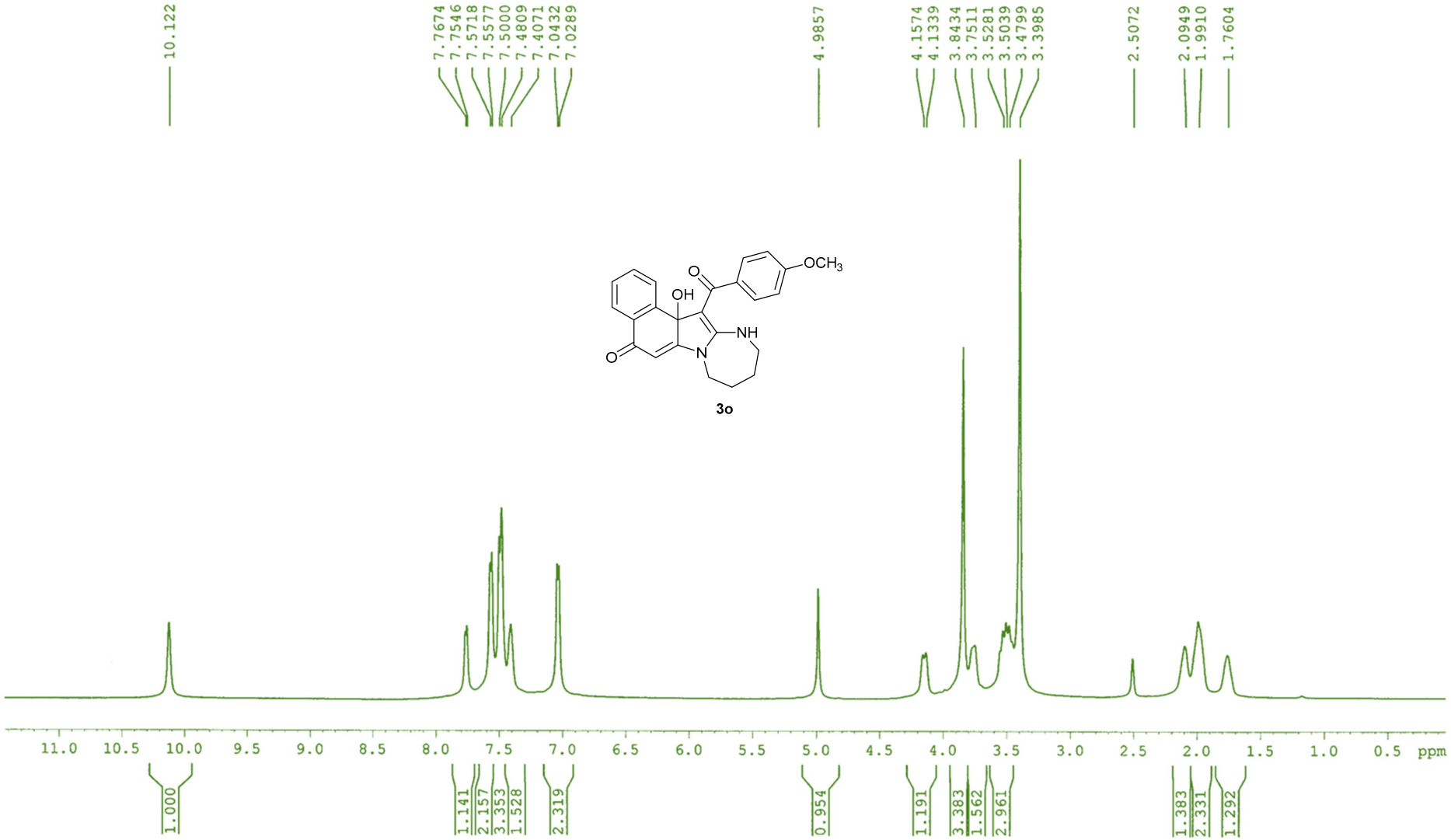


Fig. S29 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3o**

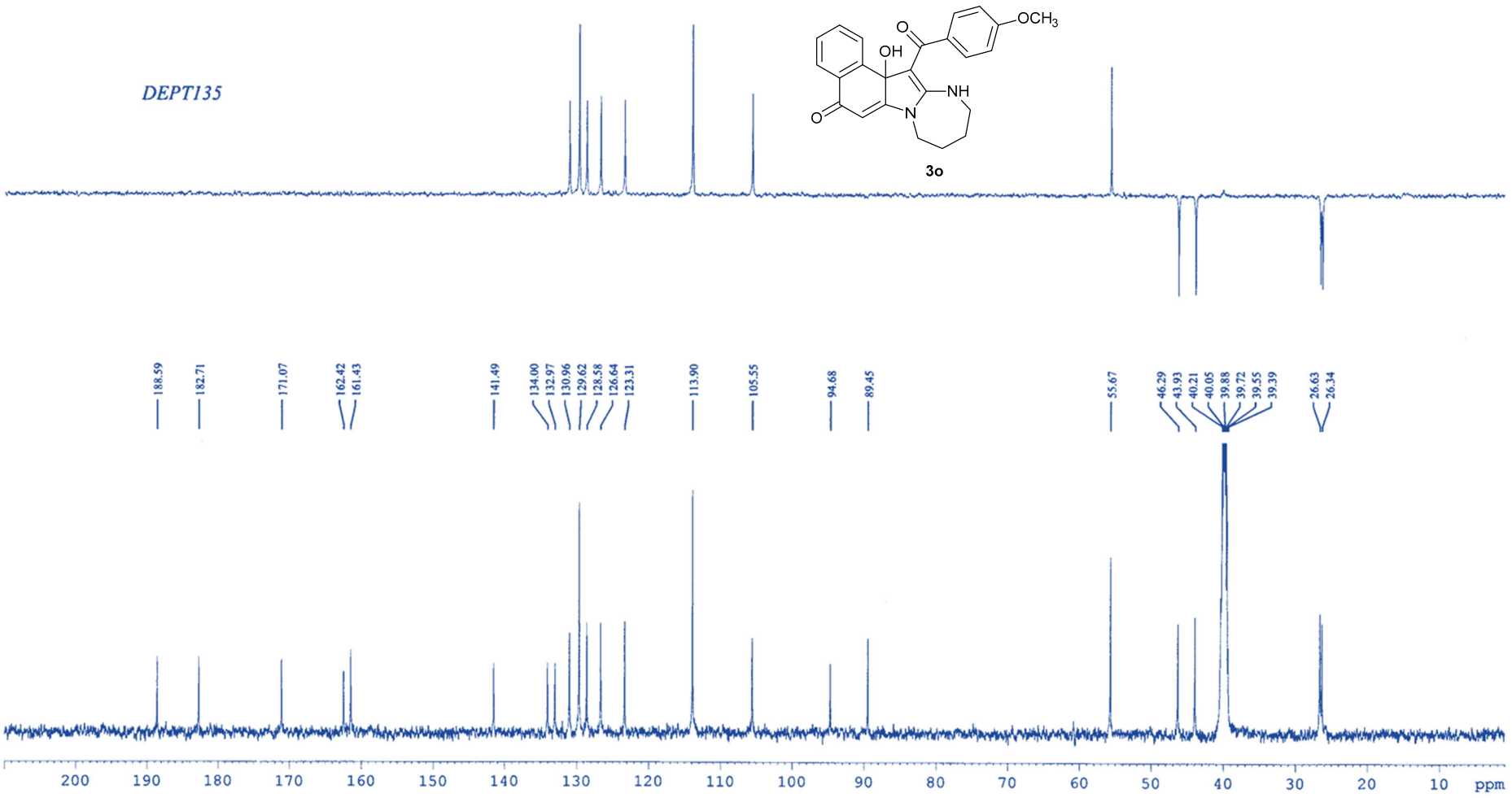


Fig. S30 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3o**

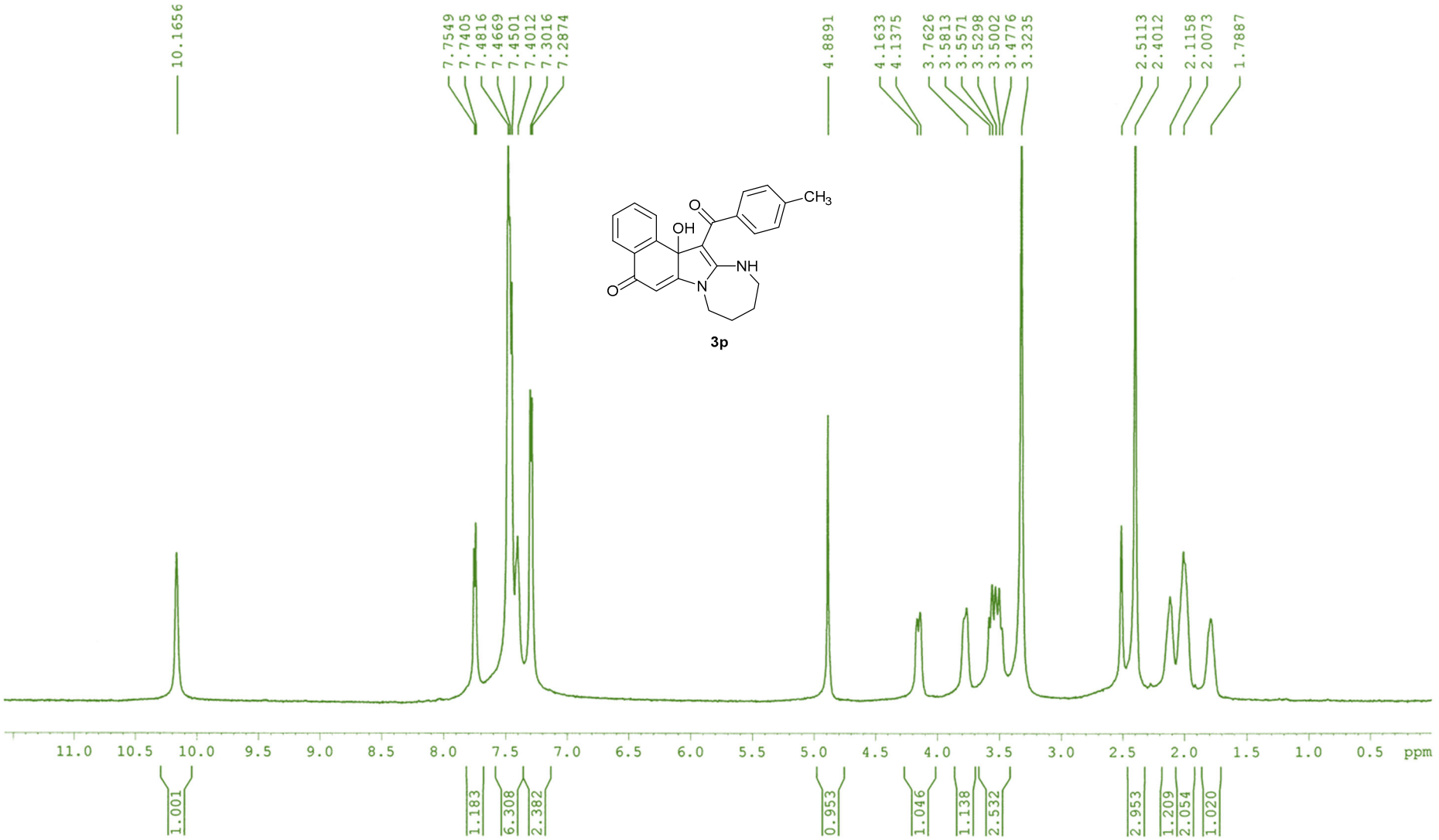


Fig. S31 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3p**

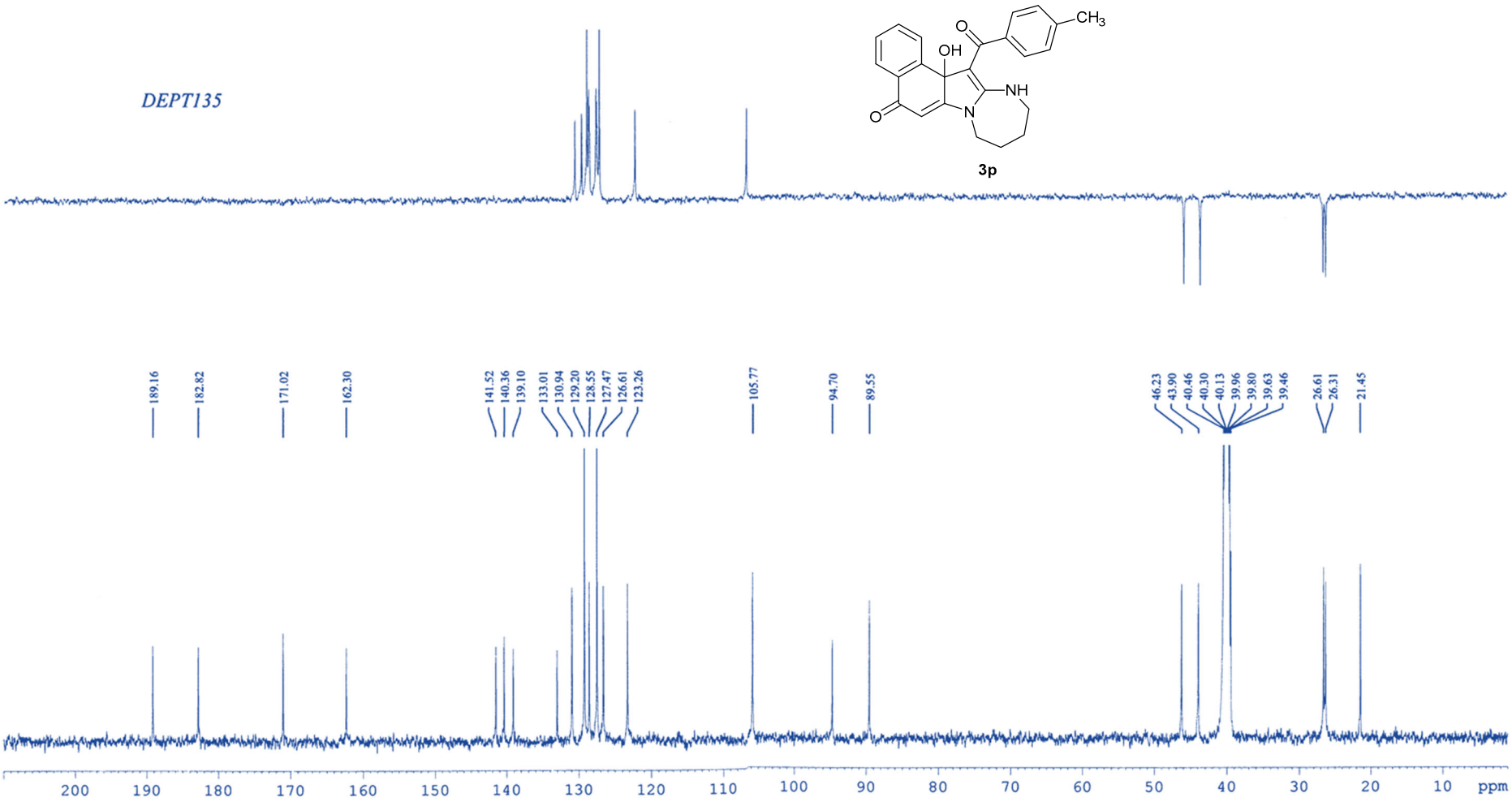


Fig. S32 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3p**

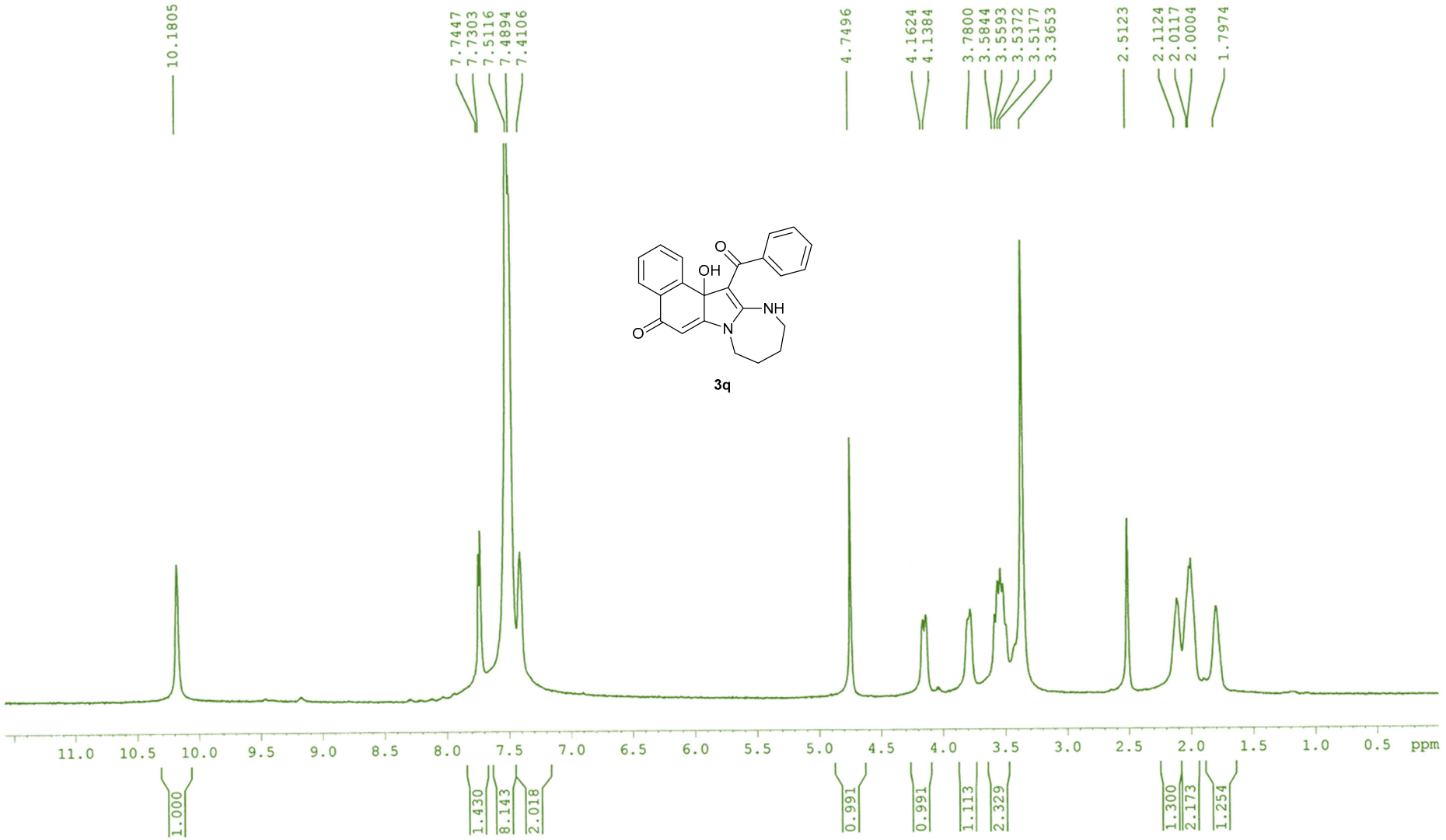


Fig. S33 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3q**

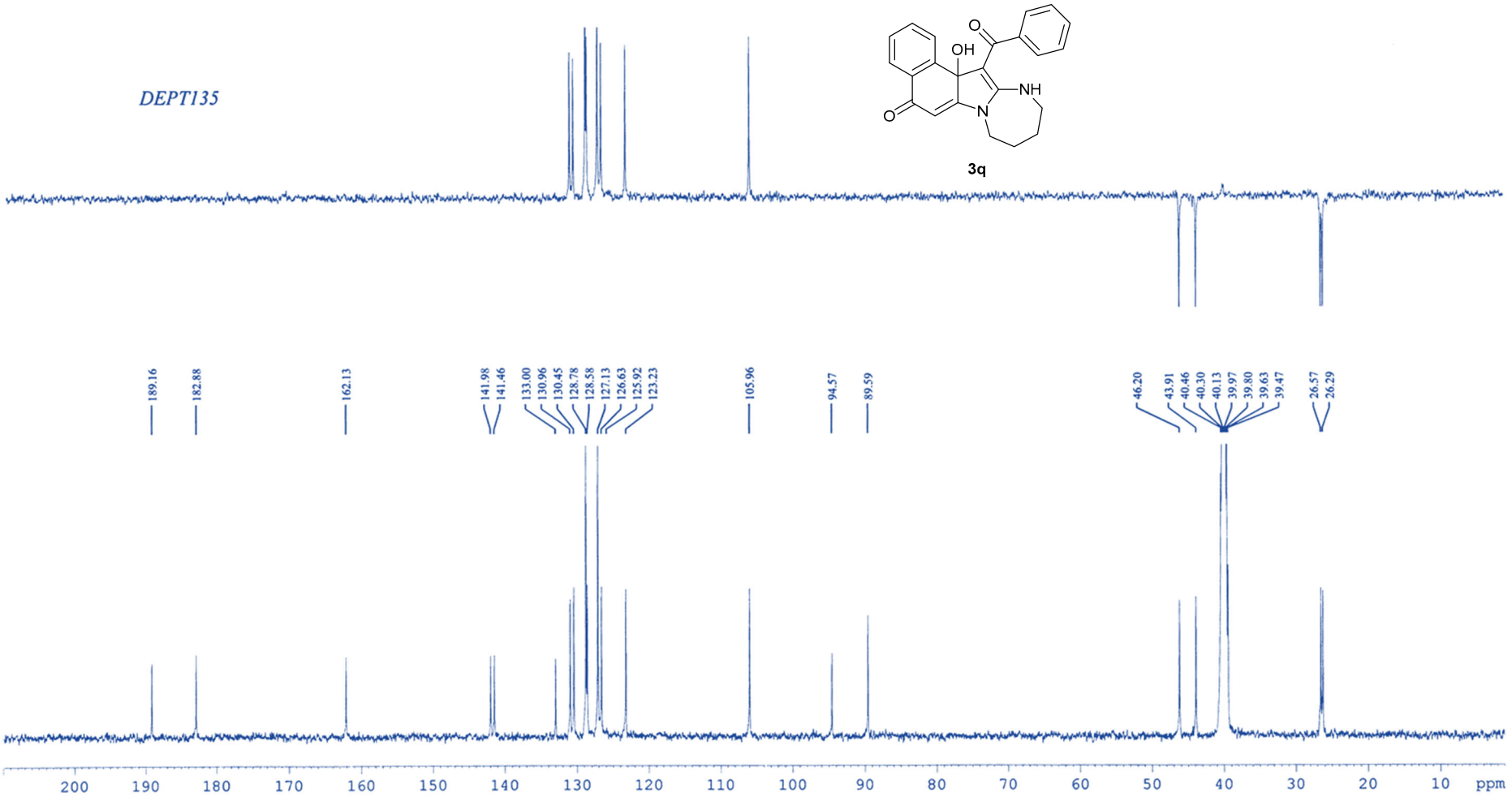


Fig. S34 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3q**

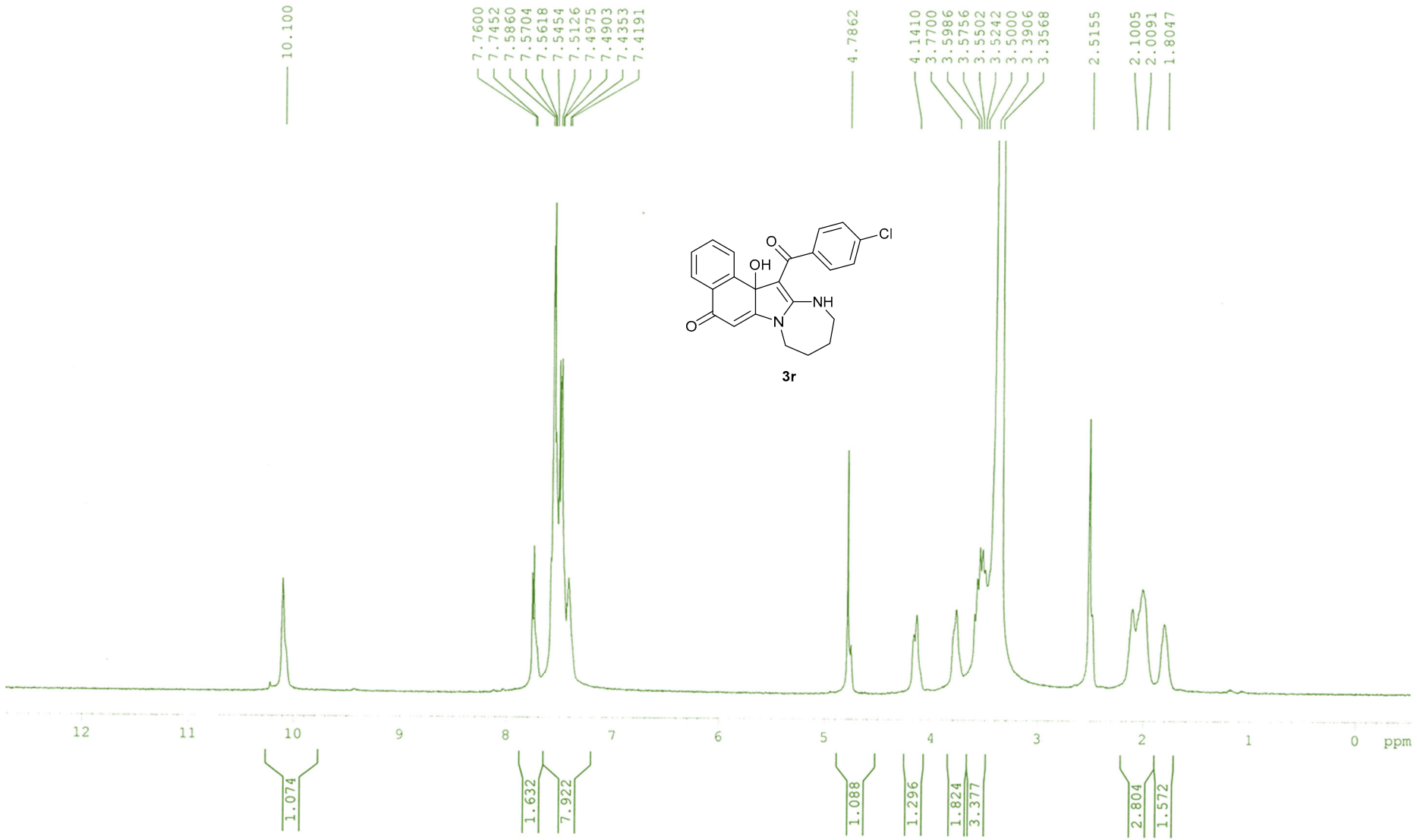


Fig. S35 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3r**

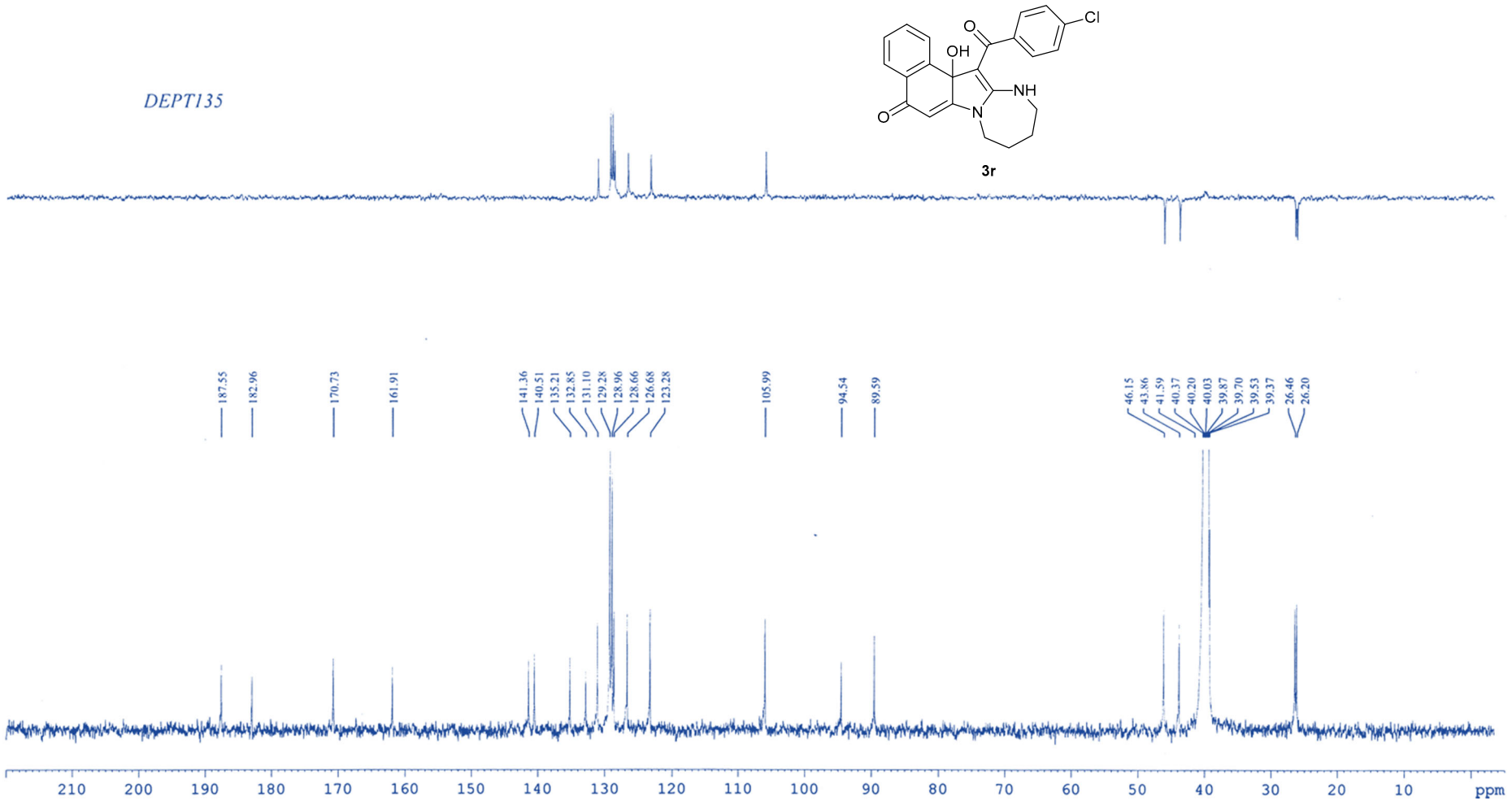


Fig. S36 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3r**

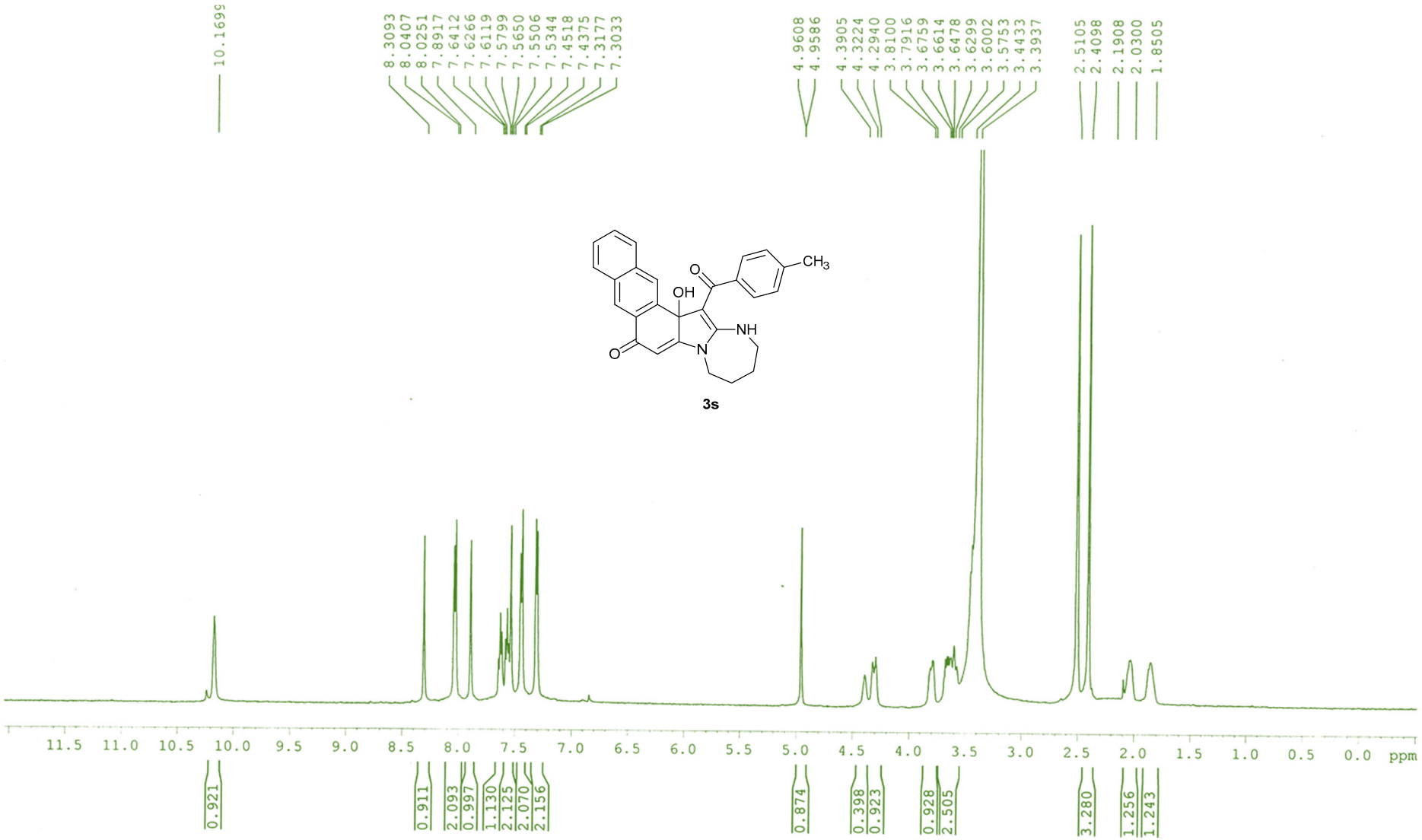


Fig. S37 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3s**

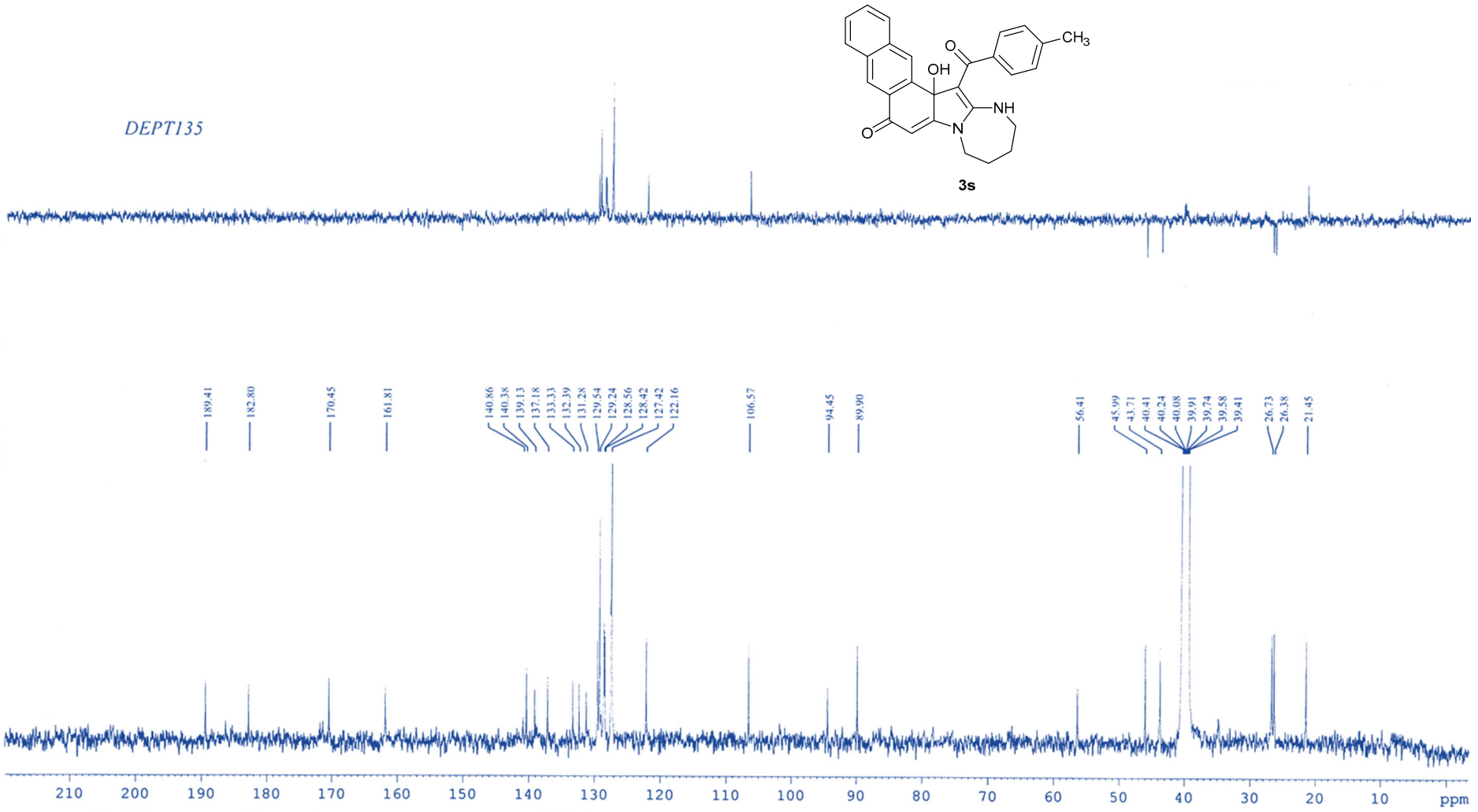


Fig. S38 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3s**

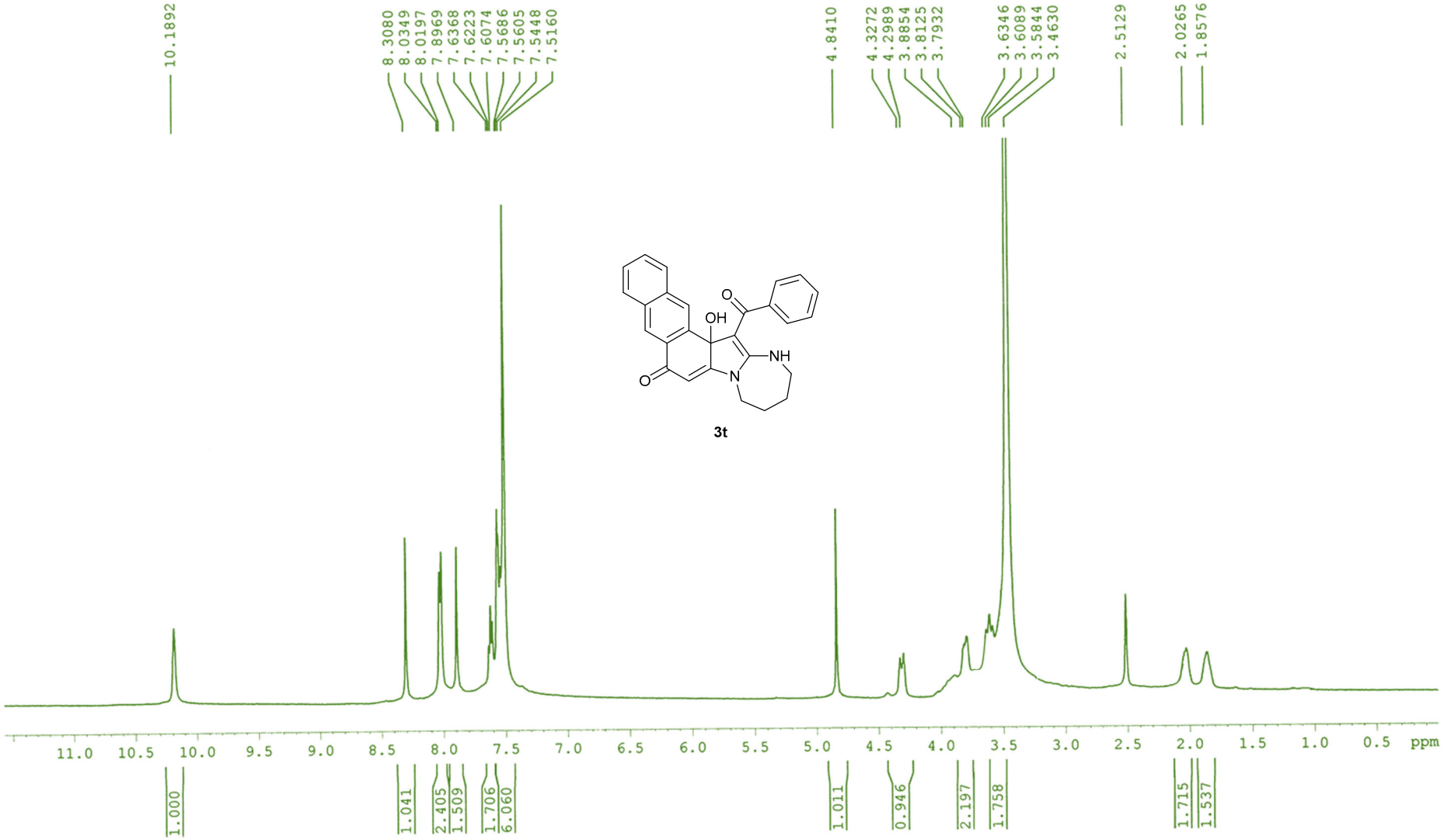


Fig. S39 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3t**

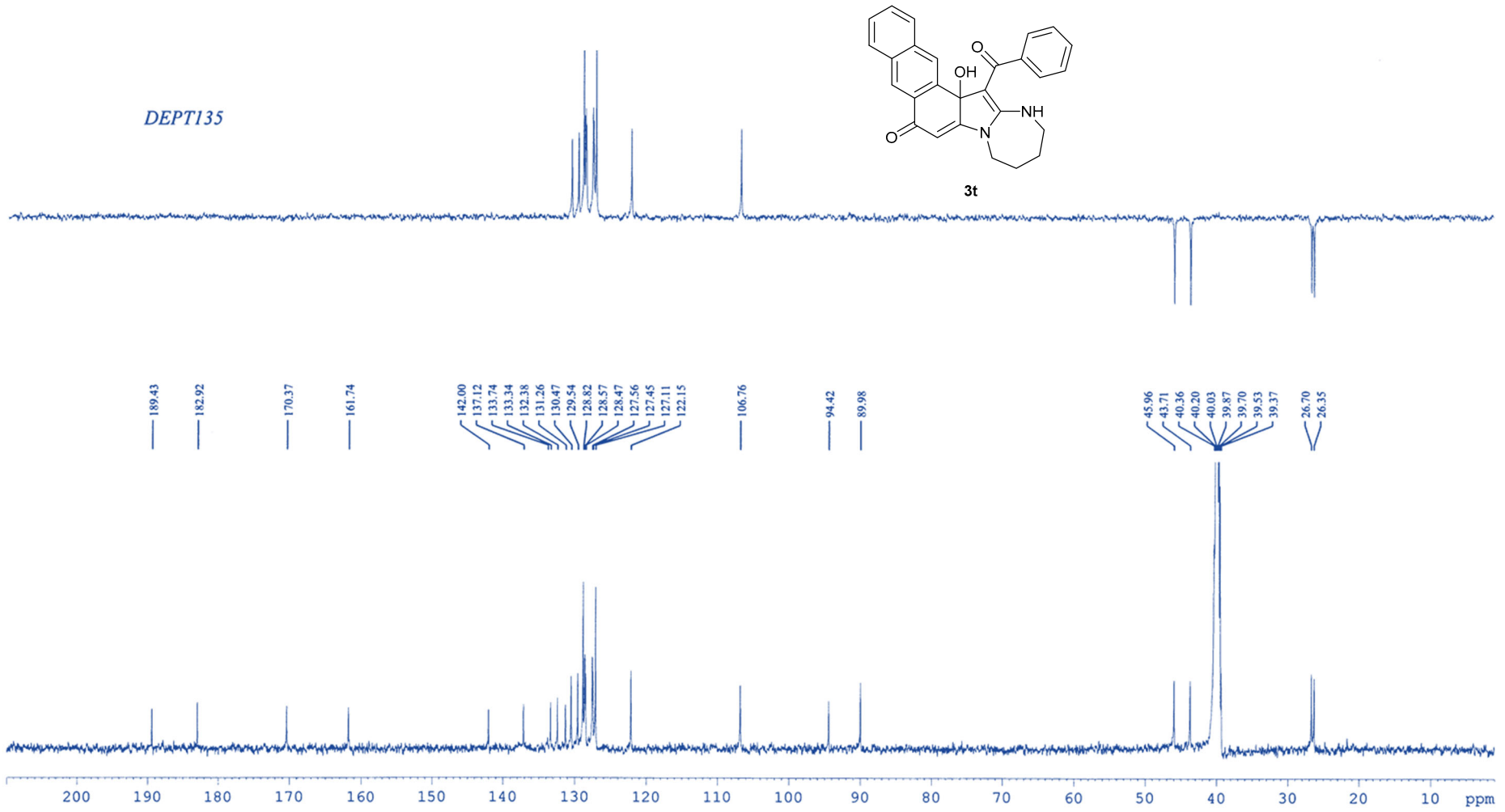


Fig. S40 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3t**

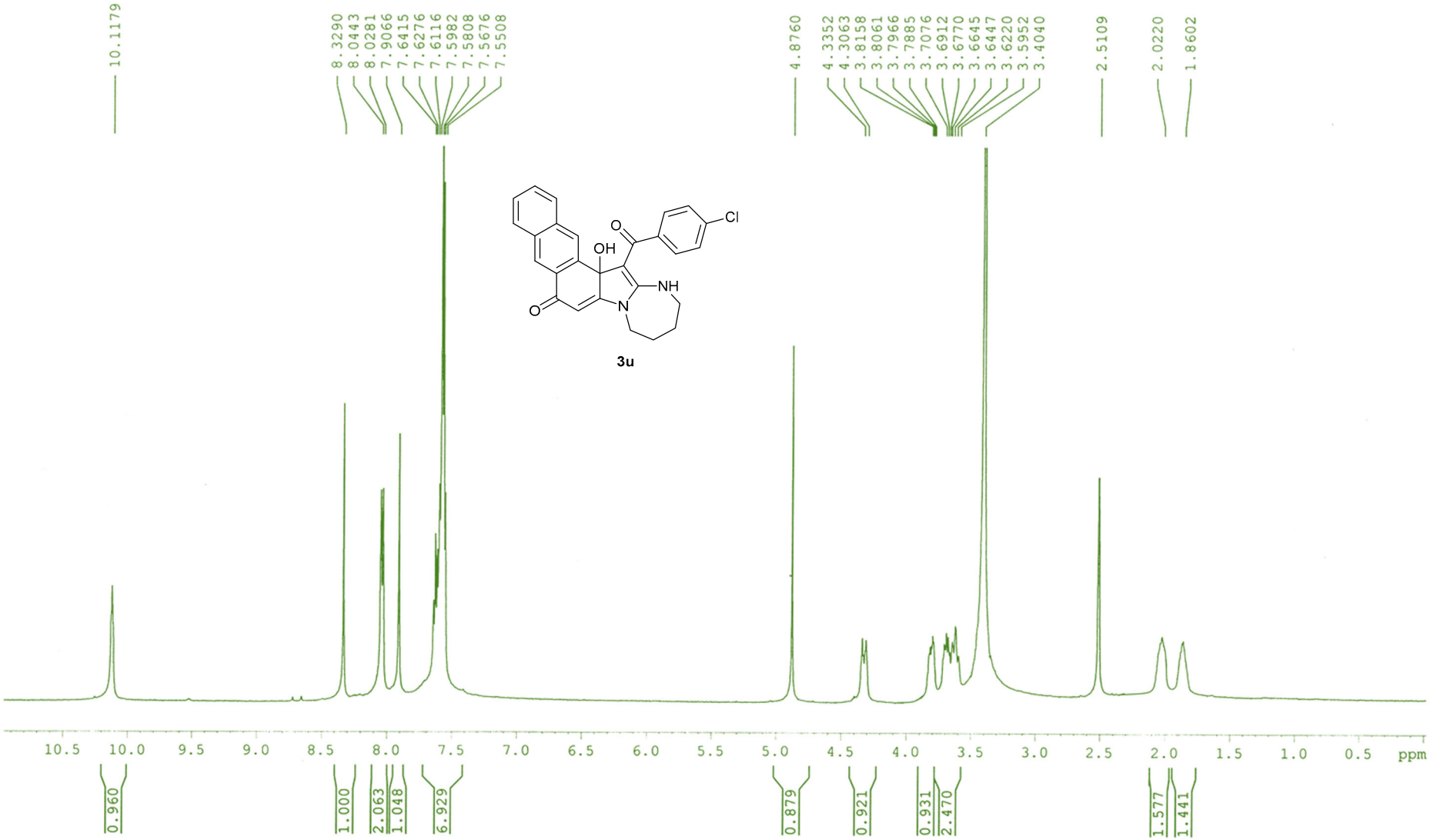


Fig. S41 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3u**

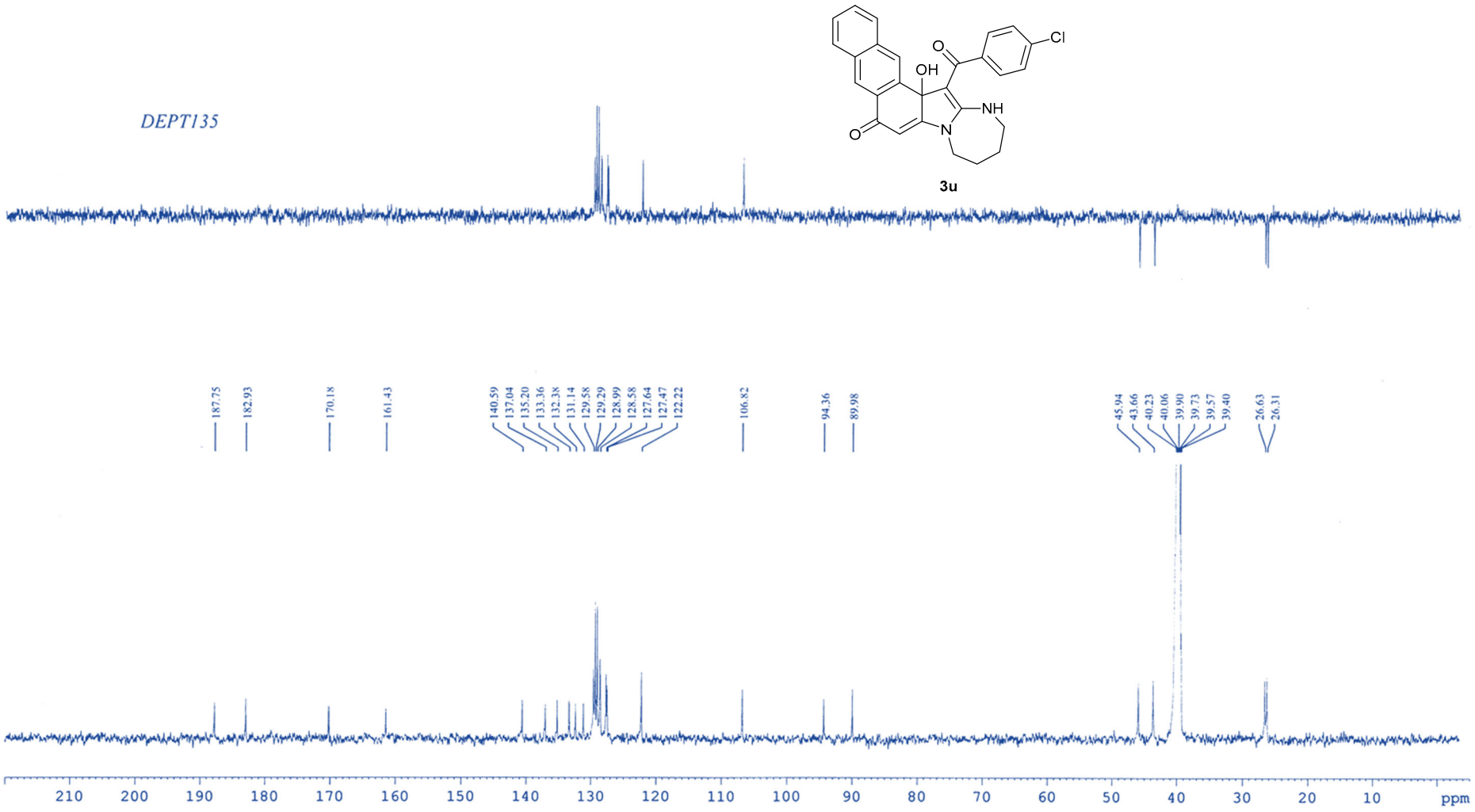


Fig. S42 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3u**

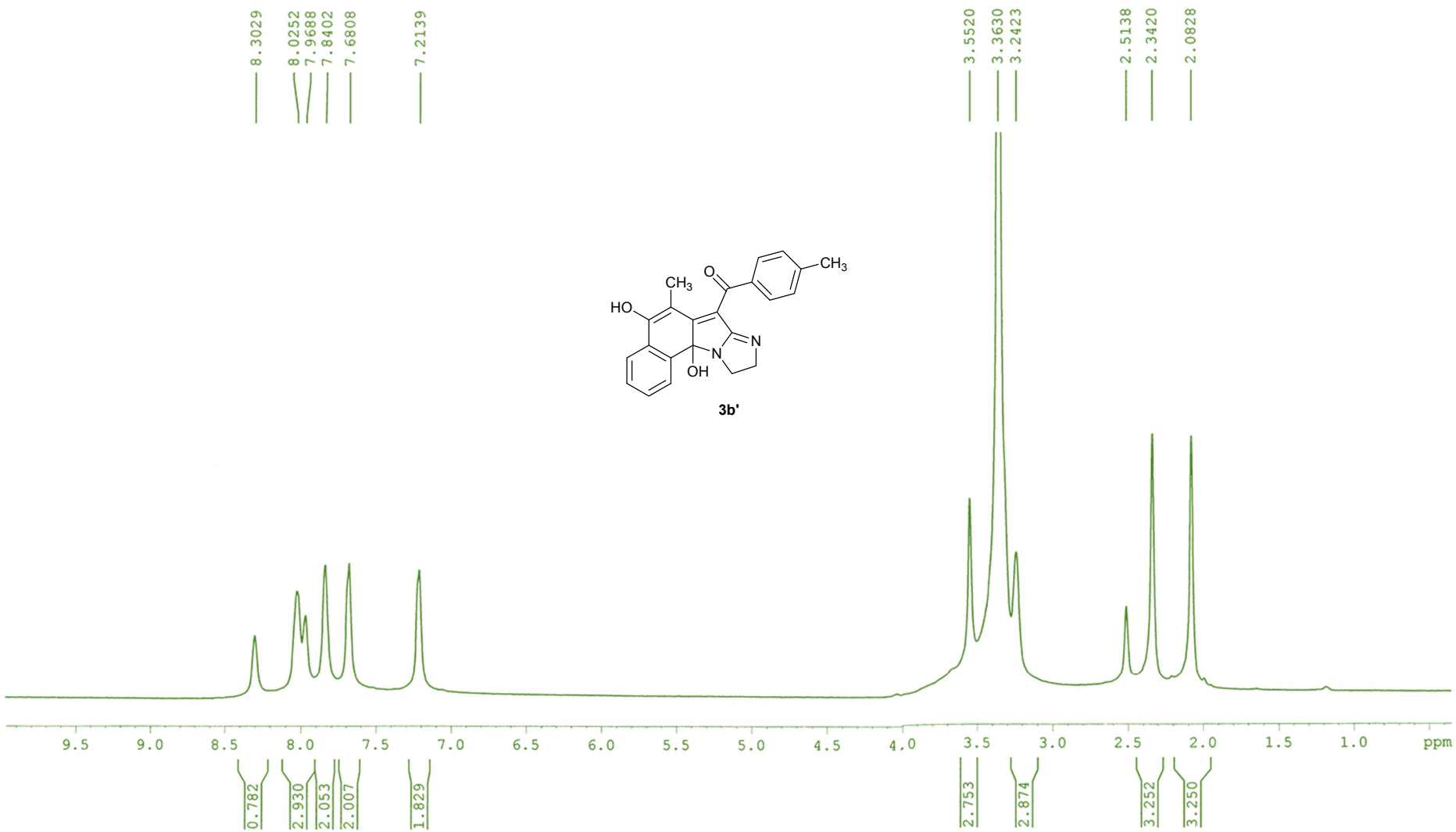


Fig. S43 ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **3b′**

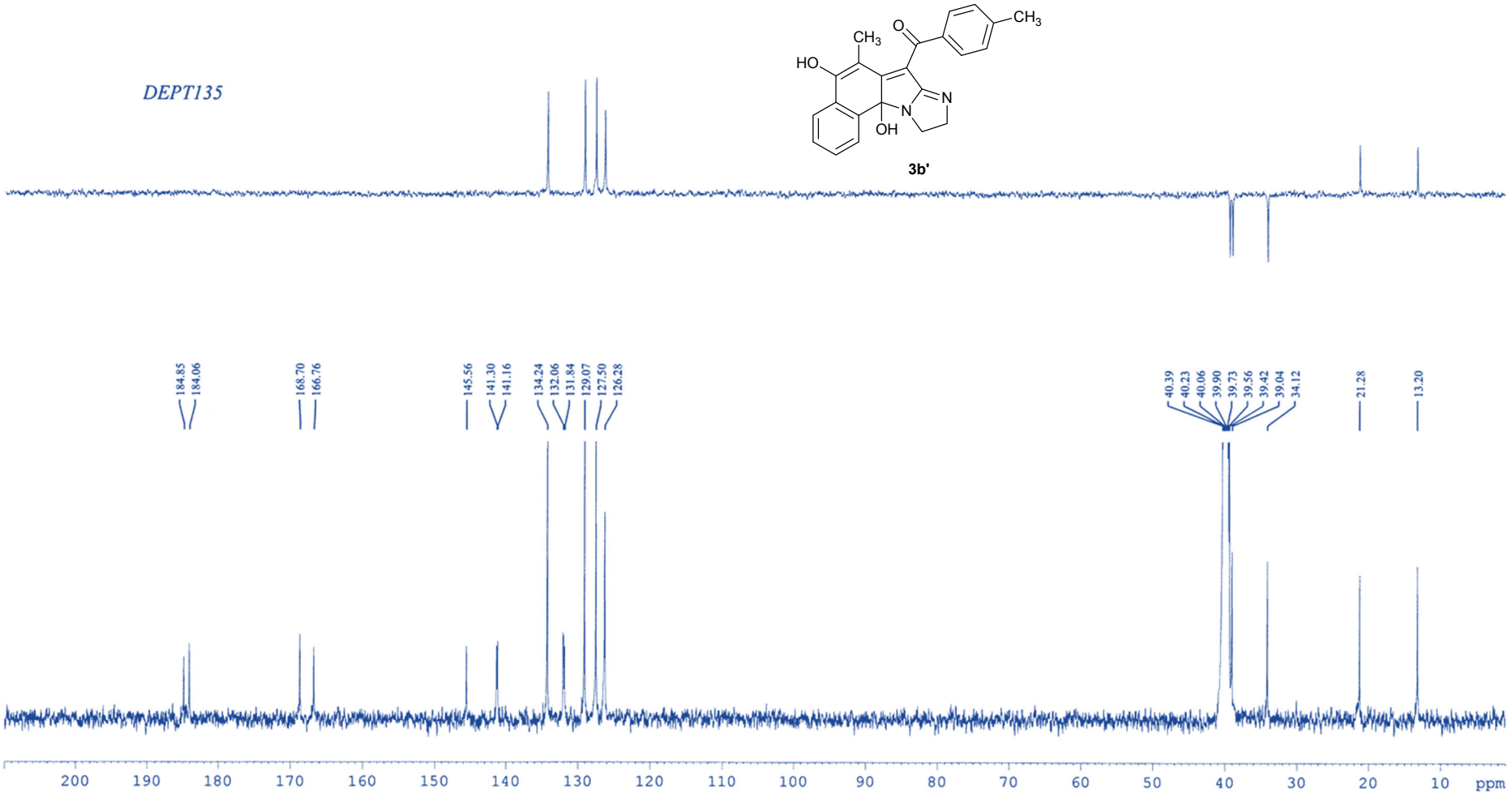


Fig. S44 ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of compound **3b′**

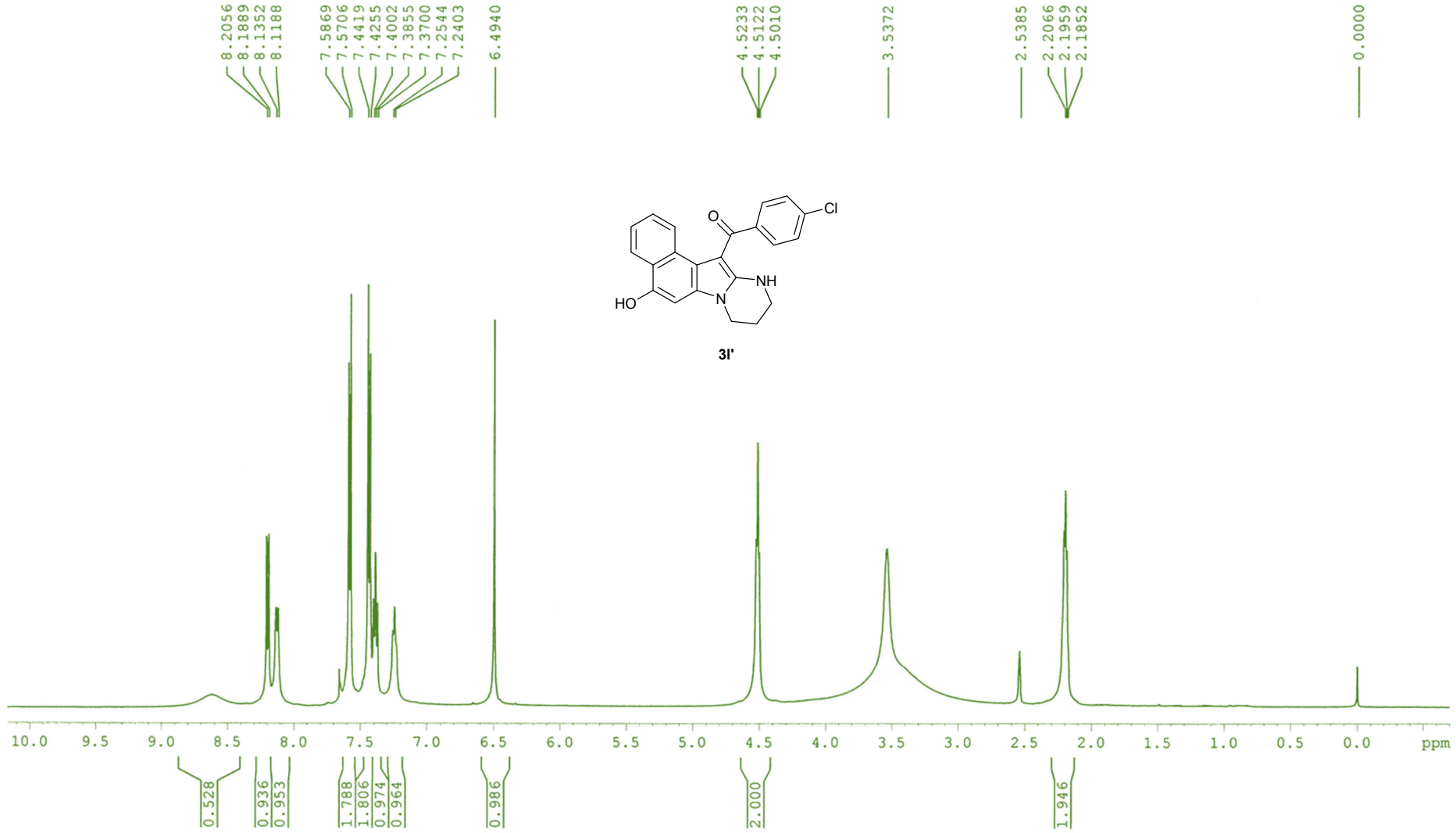


Fig. S45 ^{1}H NMR (500 MHz, $CDCl_3$+DMSO-d_6) spectrum of compound **3l′**

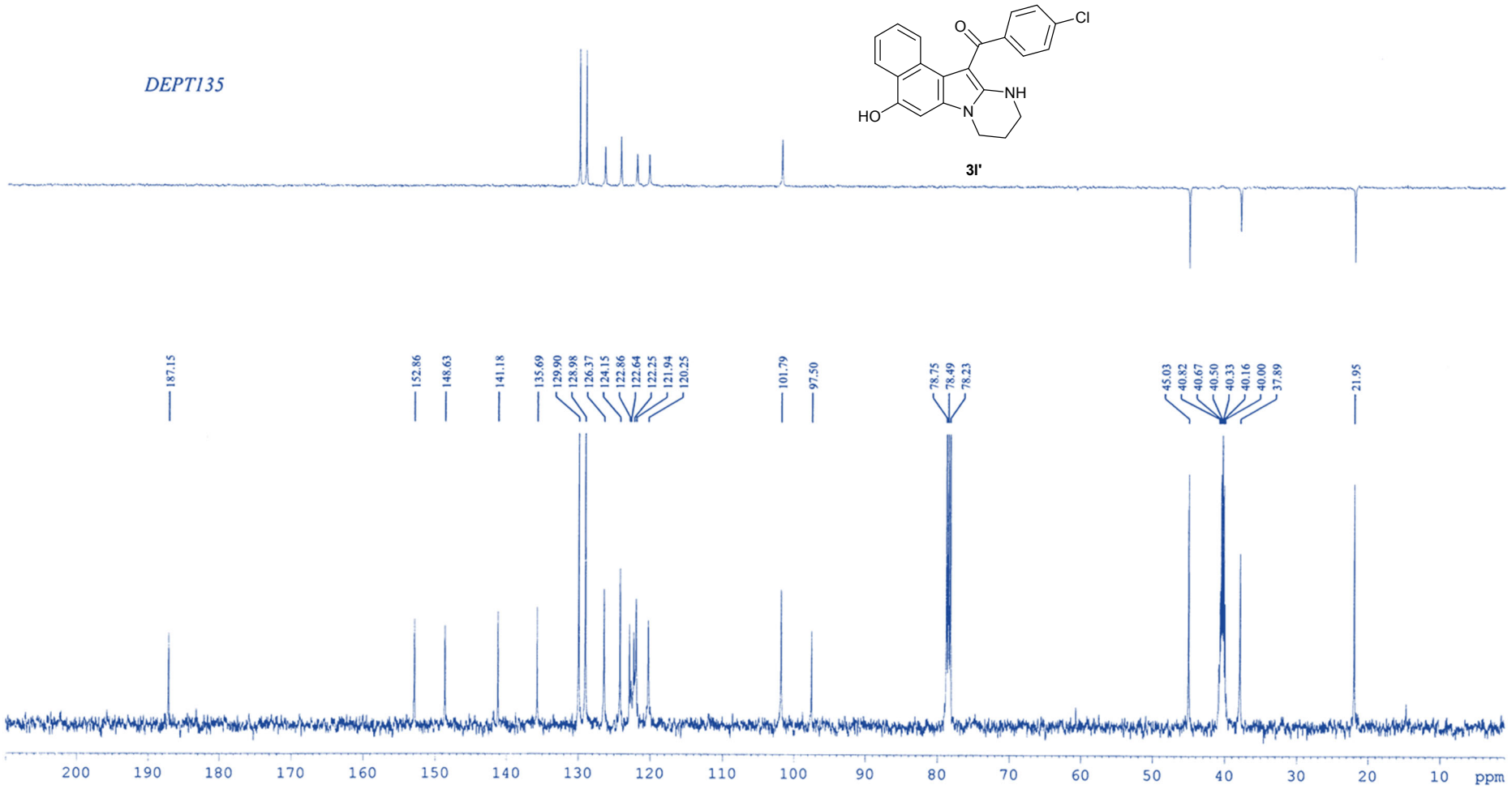


Fig. S46 ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6) spectrum of compound **3l′**

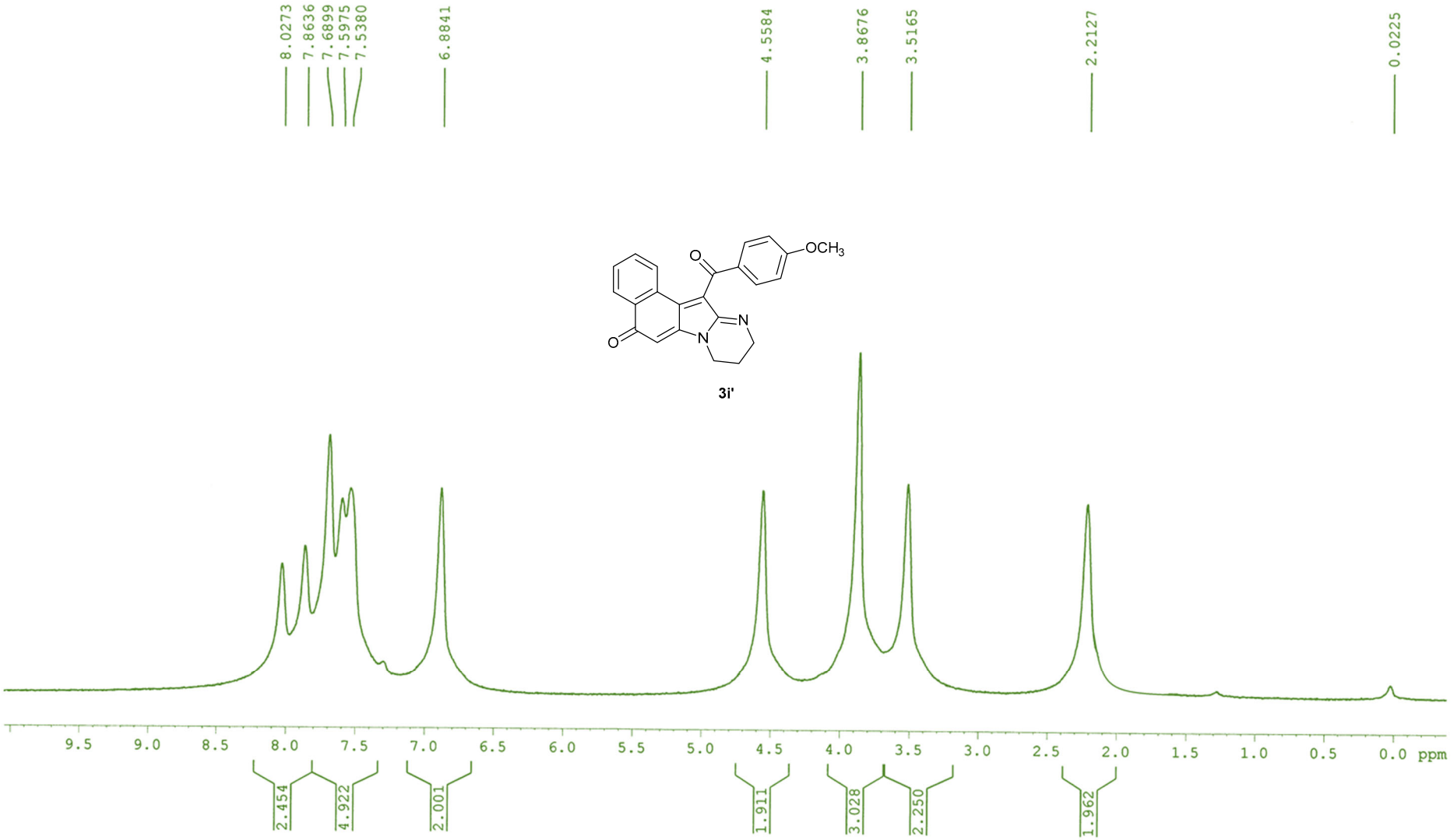


Fig. S47 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3i′**

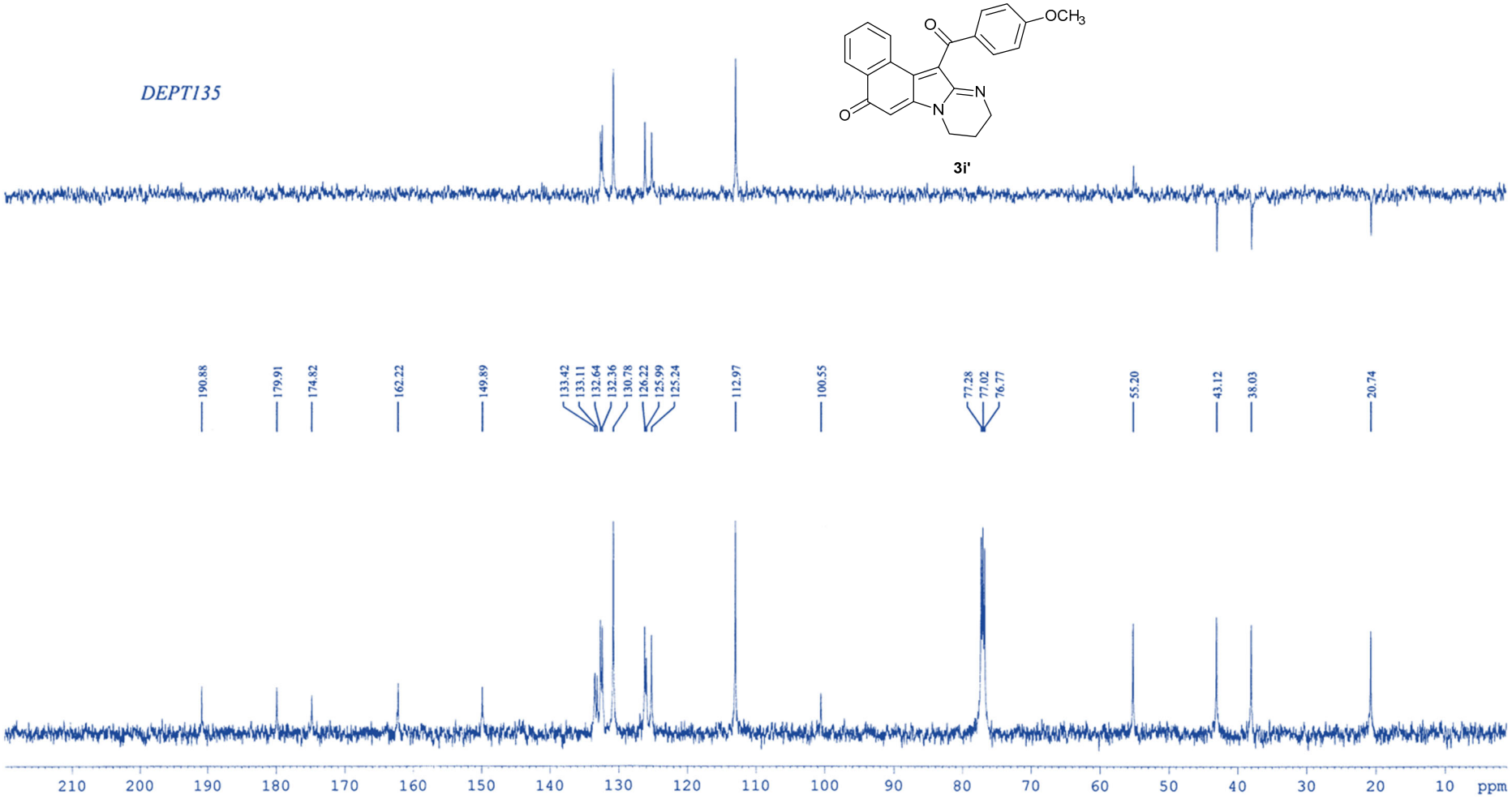
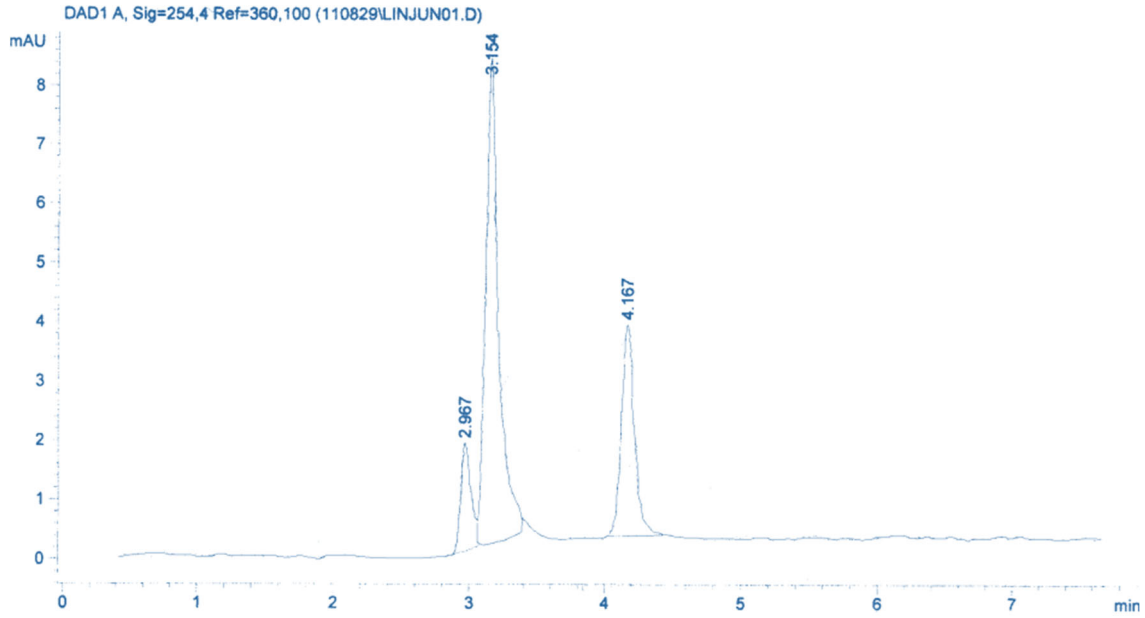


Fig. S48 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **3i′**

II HPLC Profile of Compounds 3b and 3b′



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.967	PV	0.0808	9.82429	1.82460	11.0188
2	3.154	VB	0.0973	55.87205	8.22089	62.6655
3	4.167	BB	0.0987	23.46288	3.56978	26.3157
Totals :				89.15922	13.61527	

Fig. S49 HPLC profile of compounds **3b** and **3b′**

III 2D NMR Spectra of Compound 3o

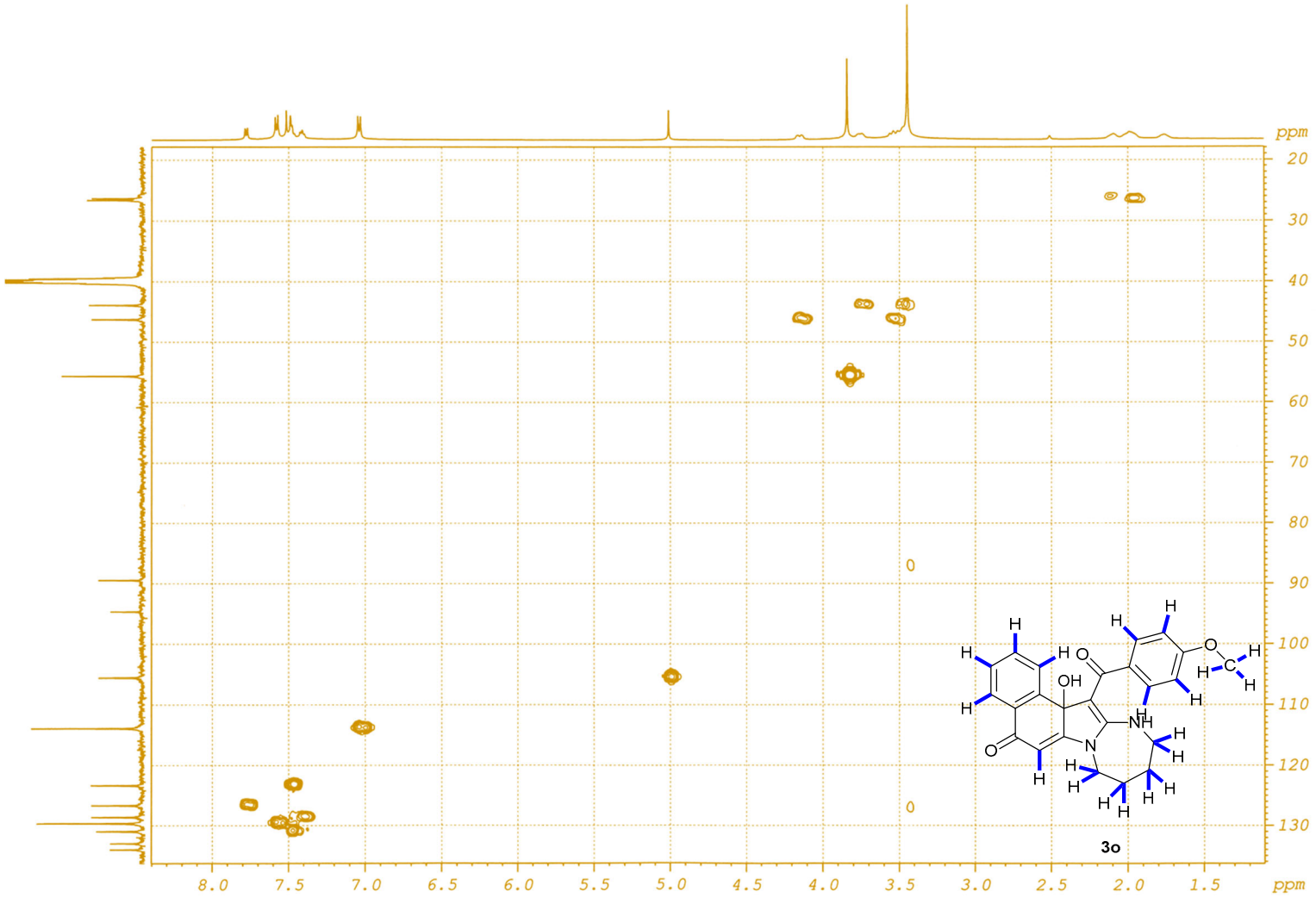


Fig. S50 HSQC (500 MHz, DMSO-d_6) correlations (—) of compound **3o**

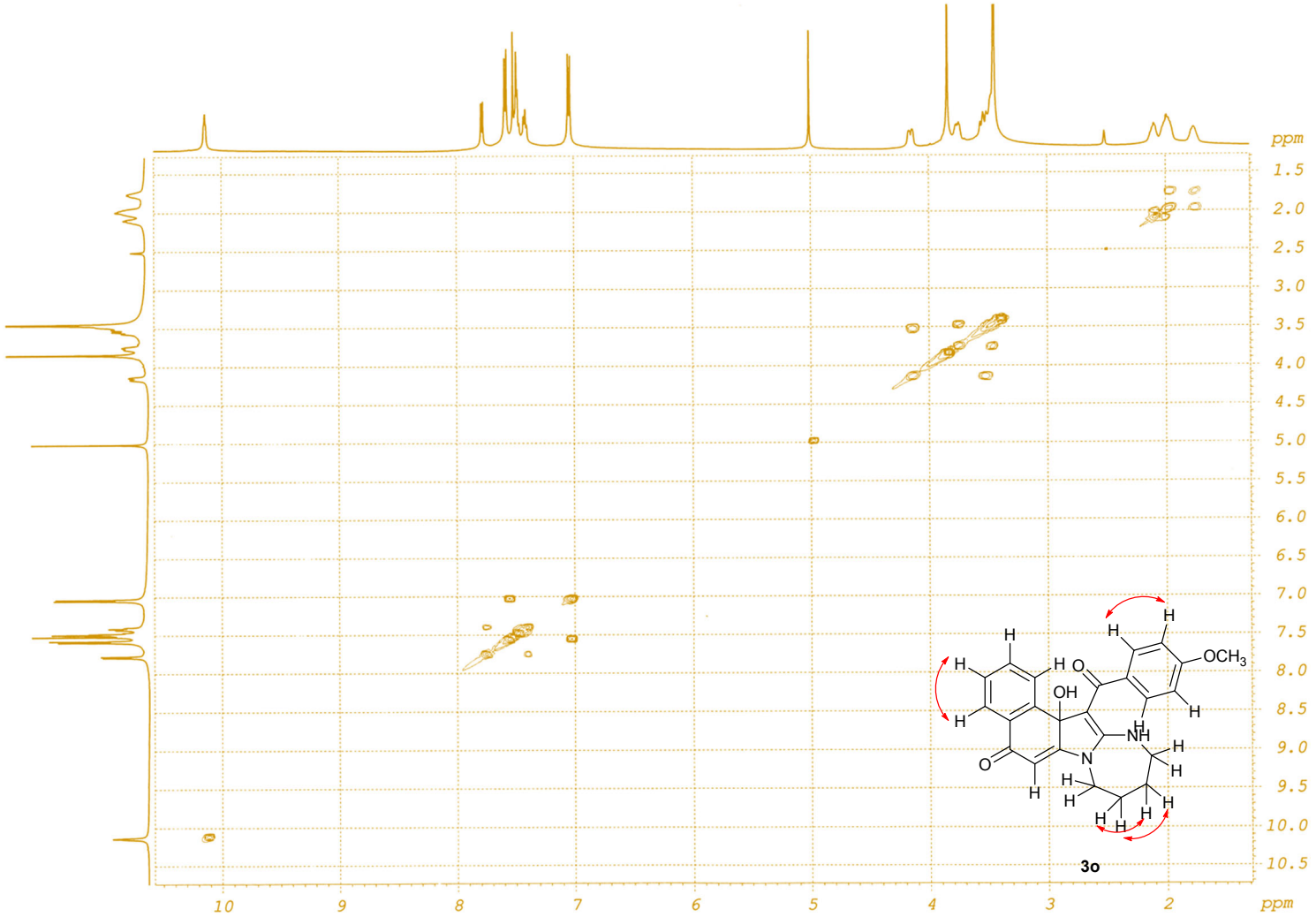


Fig. S51 COSY (500 MHz, DMSO-d_6) correlations (↔) of compound **3o**

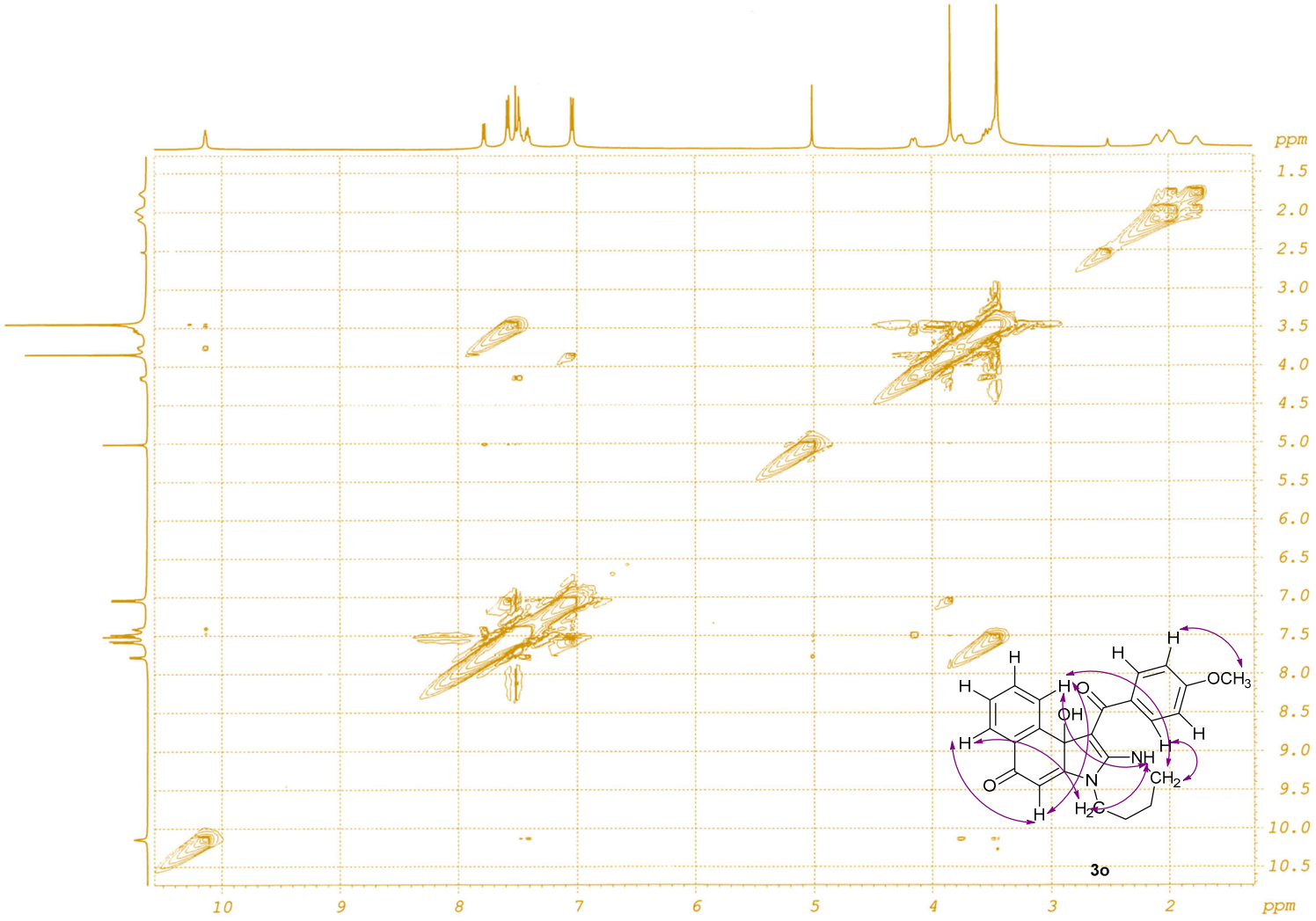


Fig. S52 NOESY (500 MHz, DMSO-d_6) correlations (↔) of compound **3o**

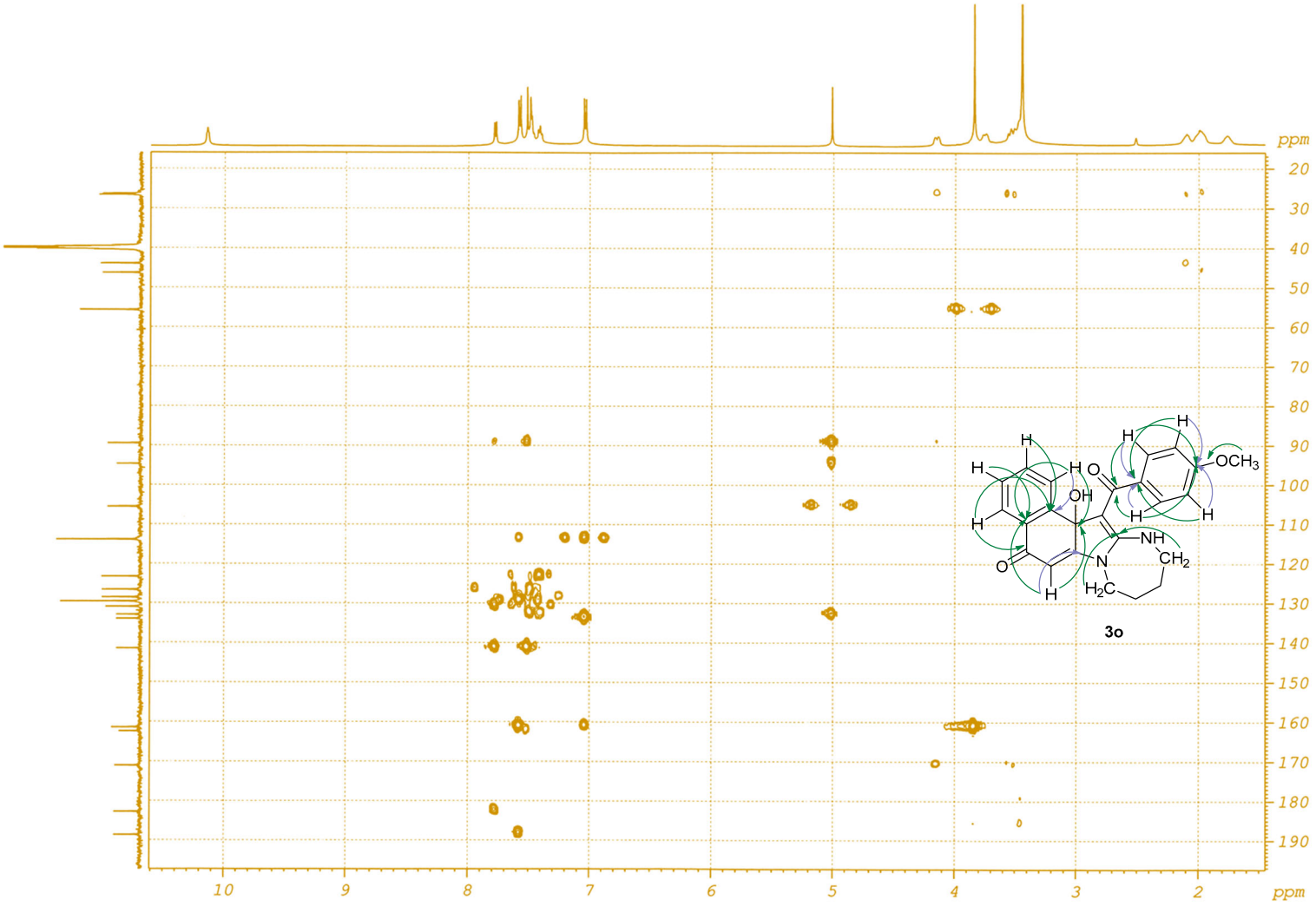


Fig. S53 HMBC (500 MHz, DMSO-d_6) correlations ($^2J_{C–H}$: →; $^3J_{C–H}$: →) of compound **3o**

IV Geometries and Energies for All Optimized Starting Materials, Transition States, Intermediates, and Target Materials

Single Point Energy[■,Δ] (E_{M06}, in Hartree)

Zero-point correction (E_0, in Hartree)

Thermal correction to Enthalpy (H, in Hartree)

Thermal correction to Gibbs Free Energy (G, in Hartree)

Sum of electronic and zero-point Energies ($E_{M06}+E_0$, in Hartree)

Sum of electronic and thermal Enthalpies ($E_{M06}+H$, in Hartree)

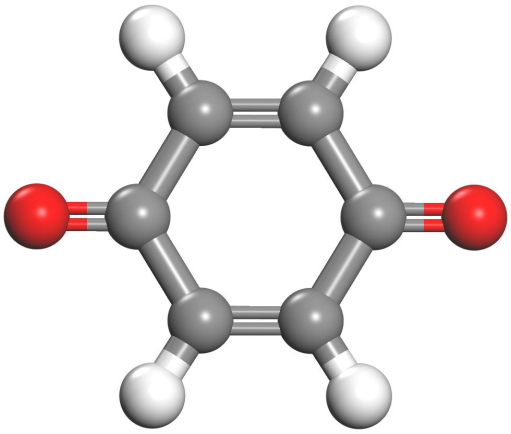
Sum of electronic and thermal Free Energies ($E_{M06}+G$, in Hartree)

■ The single-point energies and solvent effects were computed at the M06/6-31+G(d) level

Δ The single-point energies and solvent effects were computed at the M06/6-311+G(2d,2p) level

Table S1 Cartesian coordinates, optimized geometry, and energies of **A1a**

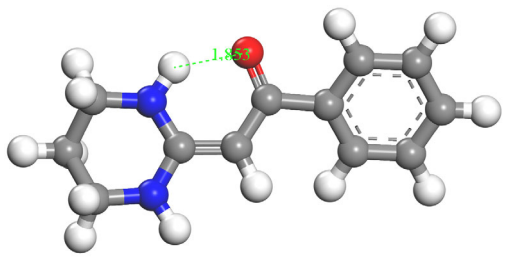
Benzoquinone (A1a)			
E_{M06}	E_0	H	G
▪-381.2367509 △-381.3279171	0.085055 $E_{M06}+E_0$ -381.151695	0.092314 $E_{M06}+H$ -381.144437	0.055685 $E_{M06}+G$ -381.181066



Atoms	*x*	*y*	*z*
C	0.0000000	0.0000000	1.4339450
C	0.0000000	1.2659860	0.6698220
C	0.0000000	1.2659860	-0.6698220
C	0.0000000	0.0000000	-1.4339450
C	0.0000000	-1.2659860	-0.6698220
C	0.0000000	-1.2659860	0.6698220
O	0.0000000	0.0000000	2.6584980
O	0.0000000	0.0000000	-2.6584980
H	0.0000000	2.1830690	1.2563340
H	0.0000000	2.1830690	-1.2563340
H	0.0000000	-2.1830690	-1.2563340
H	0.0000000	-2.1830690	1.2563340

Table S2 Cartesian coordinates, optimized geometry, and energies of **A2g**

1-Phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethan-1-one (A2g)			
E_{M06}	E_0	H	G
▪-650.019281 △-650.1793949	0.242735 $E_{M06}+E_0$ -649.776546	0.256790 $E_{M06}+H$ -649.762491	0.201653 $E_{M06}+G$ -649.817628

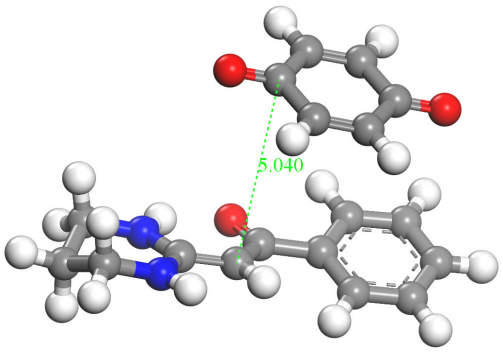


Atoms	*x*	*y*	*z*
N	-1.9705981	-1.0238827	0.0802667
C	-3.3925021	-1.3264307	0.0515347
C	-4.1864021	-0.1045317	0.4722567
C	-3.7551691	1.0851993	-0.3641103
N	-2.3109751	1.2381173	-0.2693493
C	-1.4569061	0.2030243	-0.0993533
C	-0.0628251	0.4294403	-0.0973053
C	0.8852959	-0.5984147	0.0689547
C	2.3413719	-0.2313407	0.0475717
C	3.2744299	-1.2282887	-0.2585453
C	4.6361549	-0.9464357	-0.2930983
C	5.0907019	0.3399433	-0.0056003
C	4.1726449	1.3387683	0.3148707

C	2.8097249	1.0561143	0.3376677
O	0.5919719	-1.8198747	0.2164107
H	0.2630339	1.4517503	-0.2721913
H	-1.2596211	-1.7551967	0.1729597
H	-3.5753131	-2.1691167	0.7276117
H	-3.6918831	-1.6446937	-0.9599543
H	-4.0070711	0.1077433	1.5358637
H	-5.2589621	-0.2876737	0.3418077
H	-4.2195821	2.0109763	-0.0075123
H	-4.0578741	0.9427683	-1.4141223
H	-1.9028021	2.1464403	-0.4477553
H	2.9114319	-2.2316227	-0.4732113
H	5.3468159	-1.7331717	-0.5428533
H	6.1565019	0.5626183	-0.0258543
H	4.5193259	2.3431223	0.5540877
H	2.1090799	1.8446493	0.6089527

Table S3 Cartesian coordinates, optimized geometry, and energies of **ACom 1**

ACom 1			
E_{M06}	E_0	H	G
▪-1031.2581085 $^{\Delta}$-1031.5092725	0.329464	0.351638	0.275113
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.928644	-1030.906470	-1030.982995

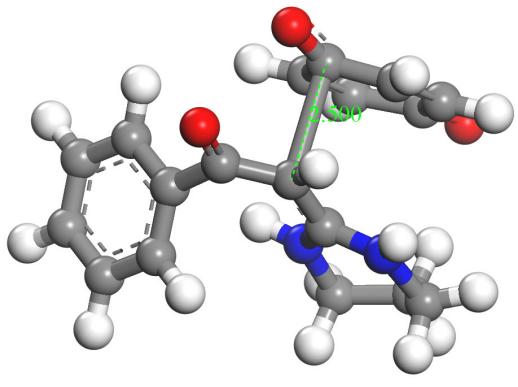


Atoms	*x*	*y*	*z*
N	2.0053375	-1.7459751	-1.5091237
C	3.3569665	-2.2811911	-1.4683737
C	4.3212505	-1.2943881	-2.0980257
C	4.1319235	0.0681949	-1.4595397
N	2.7311635	0.4513369	-1.5579247
C	1.7110285	-0.4365591	-1.5149437
C	0.3752315	0.0213909	-1.4896107
C	-0.7345025	-0.8420871	-1.4095407
C	-2.1059425	-0.2346361	-1.3322677
C	-3.1422135	-1.0044911	-0.7916857
C	-4.4320905	-0.4940201	-0.6872327
C	-4.7125515	0.7938969	-1.1412257
C	-3.6931485	1.5642279	-1.6985047
C	-2.4001635	1.0559269	-1.7883397
O	-0.6521145	-2.1035081	-1.3703127
H	0.2339395	1.0991459	-1.4778467
H	1.1791205	-2.3486801	-1.4458667

	H	3.3614485	-3.2362931	-2.0054777
	H	3.6503175	-2.4876211	-0.4265027
	H	4.1319585	-1.2245941	-3.1785747
	H	5.3533745	-1.6354651	-1.9589267
	H	4.7300115	0.8320509	-1.9679357
	H	4.4488905	0.0428249	-0.4041537
	H	2.4896695	1.4321259	-1.4982077
	H	-2.9149805	-2.0140031	-0.4532927
	H	-5.2229825	-1.1040651	-0.2527717
	H	-5.7223015	1.1946669	-1.0656507
	H	-3.9056955	2.5660149	-2.0691337
	H	-1.6224545	1.6673089	-2.2437937
	C	0.7534955	0.4469419	3.5184373
	C	0.5000065	1.8555409	3.1460673
	C	-0.7453235	2.3479659	3.1079613
	C	-1.9116125	1.5032699	3.4449063
	C	-1.6586065	0.0934009	3.8121503
	C	-0.4132445	-0.3990841	3.8501793
	O	1.8919265	-0.0042171	3.5498663
	O	-3.0486585	1.9582109	3.4250233
	H	1.3754645	2.4560389	2.9045823
	H	-0.9606335	3.3796879	2.8350883
	H	-2.5345265	-0.5075031	4.0506373
	H	-0.1987765	-1.4317871	4.1198873

Table S4 Cartesian coordinates, optimized geometry, and energies of **ATS 1**

ATS 1 (*i* = -36.12)			
E_{M06}	E_0	H	G
▪-1031.2469351 $^{\Delta}$-1031.497392	0.329907 $E_{M06}+E_0$ -1030.917028	0.350744 $E_{M06}+H$ -1030.896192	0.280949 $E_{M06}+G$ -1030.965986

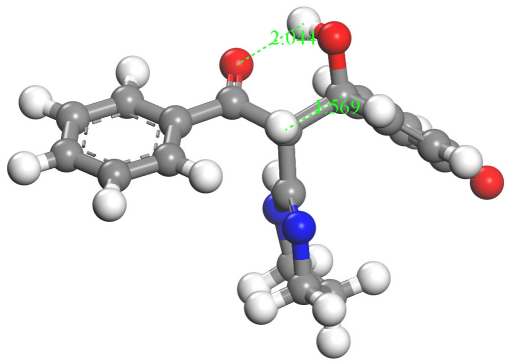


Atoms	*x*	*y*	*z*
N	1.6092104	0.8971631	-1.6520914
C	2.3445944	2.1119081	-1.3174694
C	2.1670844	2.4365631	0.1519426
C	0.6947144	2.3917481	0.5082726
N	0.1364354	1.1085521	0.0974916
C	0.5316724	0.4348501	-0.9919084
C	-0.0567116	-0.7843039	-1.4344444
C	-1.4065416	-1.2410069	-1.2971324
C	-2.4149096	-0.5615349	-0.4142294

	C	-2.8320066	0.7513351	-0.6539444
	C	-3.8439276	1.3183041	0.1170996
	C	-4.4378606	0.5824311	1.1408706
	C	-4.0313386	-0.7297859	1.3800846
	C	-3.0356066	-1.3034959	0.5952956
	O	-1.7898246	-2.2537169	-1.9081064
	H	1.9858904	2.9428811	-1.9435864
	H	3.4001984	1.9442881	-1.5597234
	H	2.7177944	1.7129161	0.7683356
	H	2.5749514	3.4313421	0.3625696
	H	0.5436824	2.4849781	1.5885786
	H	0.1475204	3.2132821	0.0199876
	H	-0.6574926	0.7430581	0.6087876
	H	-2.7363216	-2.3402709	0.7543956
	H	-4.4994116	-1.3102389	2.1735076
	H	-5.2230596	1.0293981	1.7482986
	H	-4.1699176	2.3376151	-0.0836074
	H	-2.3666386	1.3290651	-1.4534814
	C	2.7986144	-0.9991009	1.3283146
	C	1.4522364	-1.2539609	1.8645866
	C	0.5638884	-2.0036609	1.1907646
	C	0.9123044	-2.6558369	-0.0896874
	C	2.2261074	-2.3024519	-0.6705324
	C	3.1138204	-1.5510189	0.0015666
	O	3.6271824	-0.3418689	1.9627216
	H	1.2239164	-0.8106269	2.8335976
	H	-0.4258816	-2.2256569	1.5908876
	H	2.4540444	-2.7409549	-1.6424004
	H	4.1029574	-1.3237019	-0.3951534
	H	1.8697154	0.4039731	-2.4973604
	O	0.4516294	-1.2420659	-2.2845614
	H	0.2772864	-3.6303939	-0.4985364

Table S5 Cartesian coordinates, optimized geometry, and energies of **AInt 1**

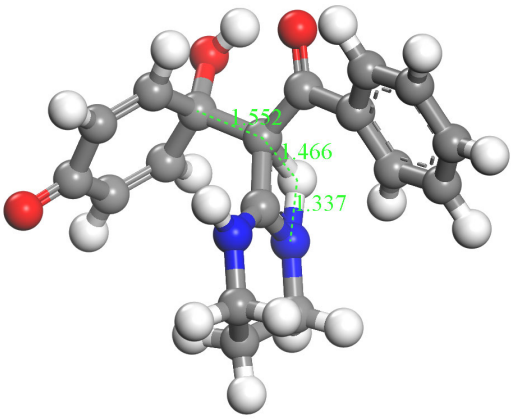
4-Hydroxy-4-(2-oxo-2-phenyl-1-(1,4,5,6-tetrahydropyrimidin-2-yl)ethyl)cyclohexa-2,5-dien-1-one (AInt 1)				
E_{M06}	E_0	H		G
▪-1031.2511098 $^{\Delta}$-1031.5027791	0.331266	0.352002		0.281821
	$E_{M06}+E_0$	$E_{M06}+H$		$E_{M06}+G$
	-1030.919844	-1030.899108		-1030.969288
	Atoms	*x*	*y*	*z*



O	-0.9657428	-2.3850032	0.9986471
C	-1.1267868	-1.4488092	0.2208421
C	0.0546842	-0.8880782	-0.5680569
C	-2.4657608	-0.8497332	0.0176971
C	0.3270682	0.5655708	-0.2245359
N	0.4665822	1.4041548	-1.1883489
N	0.3768212	0.8584508	1.1122441
C	3.1892552	-1.2740692	1.1148291
C	1.9761782	-1.7859502	0.8751921
C	4.0067982	-0.6937222	0.0385971
C	3.4784682	-0.8109062	-1.3282759
C	2.2702112	-1.3305882	-1.5651149
C	1.3329052	-1.7937482	-0.4868249
O	0.9763122	-3.1260182	-0.8403419
O	5.0938702	-0.1654782	0.2687411
C	-2.7275658	0.0948918	-0.9848189
C	-4.0104458	0.6075728	-1.1417279
C	-5.0384888	0.1889978	-0.2995489
C	-4.7857298	-0.7488322	0.7027591
C	-3.5083898	-1.2677512	0.8574981
C	0.7783462	2.7726298	-0.7958229
H	0.3405482	-3.4376562	-0.1695039
H	-1.9341608	0.4388878	-1.6459889
H	-4.2070758	1.3372758	-1.9246699
H	-5.5886228	-1.0743832	1.3613151
H	-3.2974118	-2.0017162	1.6325621
H	3.6300232	-1.2817122	2.1109511
H	1.3969222	-2.2400002	1.6802181
H	-6.0409808	0.5949028	-0.4240999
C	1.6401742	2.8307008	0.4565051
C	0.9143392	2.1328778	1.5907551
H	-0.1641898	3.3219918	-0.6235369
H	1.2774242	3.2682708	-1.6384109
H	1.8648212	3.8673578	0.7352321
H	2.5982202	2.3250668	0.2572051
H	1.5874122	1.9314978	2.4336171
H	0.0929842	2.7614168	1.9654571
H	4.1224202	-0.4606902	-2.1335009
H	1.8869122	-1.4278792	-2.5822349
H	-0.2338808	-0.8934682	-1.6294539
H	0.4155312	0.0836788	1.7639521

Table S6 Cartesian coordinates, optimized geometry, and energies of **ATS 2**

BTS 2 (*i* = -1624.12)			
E_{M06}	E_0	H	G
▪-1031.1868891 $^{\Delta}$-1031.4404043	0.326208 $E_{M06}+E_0$ -1030.860681	0.346526 $E_{M06}+H$ -1030.840363	0.277981 $E_{M06}+G$ -1030.908908



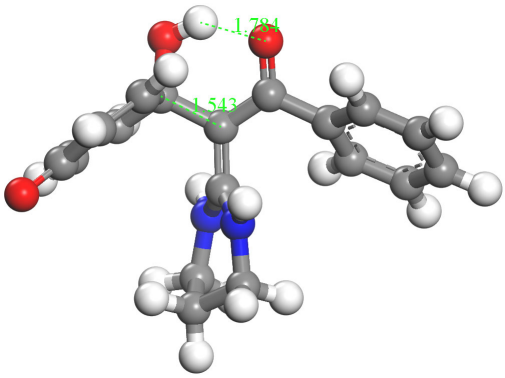
Atoms	*x*	*y*	*z*
O	-0.9785997	-2.9413714	-0.6988815
C	-0.9704147	-1.7039724	-0.5382525
C	0.2348373	-0.9265504	-0.7768575
C	-2.2488757	-1.0519054	-0.1130525
C	0.3243333	0.4873526	-0.3223935
N	0.3171603	1.1954536	-1.4282265
N	0.4298783	0.9786766	0.9096605
C	2.7473453	-1.7080404	1.4831795
C	1.7844913	-2.1824404	0.6793815
C	3.7308333	-0.7312824	0.9987355
C	3.6652613	-0.3749904	-0.4278035
C	2.6909873	-0.8366614	-1.2191025
C	1.5721663	-1.7126544	-0.7361215
O	1.5303273	-2.8197684	-1.6235905
O	4.5877463	-0.2497994	1.7415575
C	-2.6703807	0.2109916	-0.5487925
C	-3.8932467	0.7266686	-0.1275865
C	-4.7005157	-0.0001974	0.7448165
C	-4.2885347	-1.2574434	1.1836255
C	-3.0784167	-1.7837484	0.7462875
C	0.4636393	2.6497746	-1.3913285
H	0.6610803	-3.2464014	-1.4576965
H	-2.0634767	0.7868876	-1.2448065
H	-4.2187437	1.7007416	-0.4891245
H	-4.9152877	-1.8331064	1.8626595
H	-2.7569877	-2.7706874	1.0741145
H	2.8489063	-2.0319594	2.5183505
H	1.0684153	-2.9209514	1.0434775
H	-5.6519267	0.4103646	1.0790615
C	1.1660363	3.0639816	-0.1034125
C	0.4975593	2.4276206	1.1064245
H	-0.5347327	3.1113446	-1.4607445
H	1.0307003	2.9683486	-2.2733495
H	1.1525133	4.1549846	0.0022105
H	2.2188473	2.7472536	-0.1424395

	H	1.0623623	2.6248466	2.0228885
	H	-0.5200727	2.8253716	1.2432035
	H	4.4537553	0.2760656	-0.8036355
	H	2.6541013	-0.5810234	-2.2791005
	H	0.1861643	-0.0333084	-1.9381375
	H	0.4107623	0.3515336	1.7048035

Table S7 Cartesian coordinates, optimized geometry, and energies of **AInt 2**

4-Hydroxy-4-(2-oxo-2-phenyl-1-(tetrahydropyrimidin-2(1*H*)-ylidene)ethyl)cyclohexa-2,5-dien-1-one (AInt 2)

E_{M06}	E_0	H	G
▪-1031.2500128 △-1031.5027913	0.332020 $E_{M06}+E_0$ -1030.917992	0.352651 $E_{M06}+H$ -1030.897362	0.282910 $E_{M06}+G$ -1030.967103

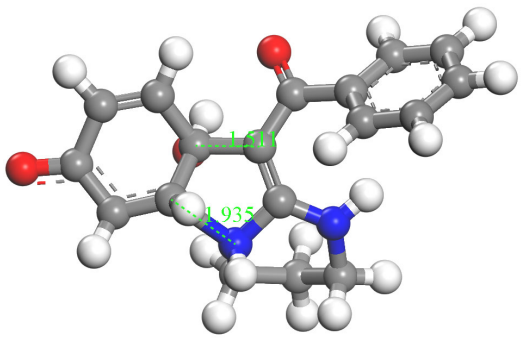


Atoms	*x*	*y*	*z*
O	-0.8862015	-3.0595796	-0.1909183
C	-0.9024905	-1.7909166	-0.2410013
C	0.2490455	-1.0261516	-0.5056983
C	-2.2344725	-1.1247186	-0.0640203
C	0.2767945	0.4102754	-0.3181523
N	0.6853555	1.2268694	-1.2929163
N	-0.0770215	0.9545474	0.8459997
C	2.9487415	-1.5318456	1.4702327
C	1.9366545	-2.1010986	0.7940187
C	3.8807235	-0.6187036	0.8078987
C	3.7000375	-0.4250896	-0.6418893
C	2.6652665	-0.9624466	-1.2974143
C	1.5922345	-1.7747176	-0.6365583
O	1.4650685	-2.9569046	-1.4104423
O	4.7941765	-0.0559386	1.4171377
C	-2.6679815	-0.0658086	-0.8693243
C	-3.9249255	0.5019984	-0.6756703
C	-4.7630935	0.0219244	0.3289107
C	-4.3435915	-1.0403766	1.1289907
C	-3.0929495	-1.6153156	0.9253097
C	1.0023615	2.6481244	-1.1437213
H	0.6229425	-3.3624136	-1.0920113
H	-2.0299185	0.3046844	-1.6721903
H	-4.2532715	1.3179244	-1.3179553
H	-4.9961645	-1.4247206	1.9116267
H	-2.7656085	-2.4536916	1.5387237

	H	3.1248645	-1.7318936	2.5267877
	H	1.2507025	-2.7954726	1.2807577
	H	-5.7446145	0.4682314	0.4815067
	C	1.0503375	3.0185254	0.3255667
	C	-0.1358895	2.3981214	1.0427097
	H	0.2392865	3.2350564	-1.6729503
	H	1.9676875	2.8339464	-1.6305413
	H	1.0407775	4.1084754	0.4307107
	H	1.9789445	2.6451924	0.7811707
	H	-0.1137305	2.5942834	2.1178307
	H	-1.0871245	2.7854174	0.6437447
	H	4.4606385	0.1650974	-1.1521253
	H	2.5620915	-0.8456356	-2.3779453
	H	0.8208055	0.8028274	-2.2028223
	H	-0.2964895	0.3219154	1.6066327

Table S8 Cartesian coordinates, optimized geometry, and energies of **ATS 3**

ATS 3 (*i* = -284.53)			
E_{M06}	E_0	H	G
▪-1031.1696251 $^{\Delta}$-1031.4215451	0.330862	0.350584	0.283815
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.838763	-1030.819041	-1030.885810

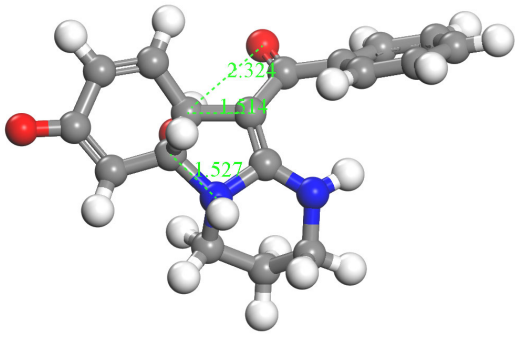


Atoms	*x*	*y*	*z*
O	0.5961188	-2.2443331	1.4564747
C	0.8800658	-1.4069941	0.5904667
C	-0.1667842	-0.5810081	0.0106477
C	2.2885708	-1.2522901	0.1358647
C	-0.0748502	0.7658479	-0.2465023
N	0.9564178	1.6366899	-0.2173723
N	-1.3421962	1.4032379	-0.5260523
C	-3.4120972	-2.5671471	-0.0150773
C	-2.0944282	-2.3903231	0.1326787
C	-4.3511112	-1.4449831	-0.3657413
C	-3.7686352	-0.2410551	-0.8649483
C	-2.3689682	-0.1918361	-0.9076023
C	-1.6218422	-0.9556481	0.1676467
O	-2.0566772	-0.4343951	1.4536337
O	-5.5768632	-1.6986661	-0.3906753
C	2.5906308	-0.8954541	-1.1838503
C	3.9149408	-0.8139261	-1.6024583
C	4.9458738	-1.0746951	-0.7016783

	C	4.6525048	-1.4302531	0.6154227
	C	3.3298698	-1.5299971	1.0297817
	C	0.6543068	3.0414559	0.1001647
	H	-1.5520242	-0.9292191	2.1205287
	H	1.7830508	-0.7011671	-1.8895523
	H	4.1428148	-0.5506831	-2.6336773
	H	5.4584248	-1.6322931	1.3186077
	H	3.0859788	-1.8161381	2.0517687
	H	5.9824148	-1.0052221	-1.0271593
	H	-3.8762232	-3.5488581	0.0829367
	C	-0.5072392	3.0928029	1.0851037
	H	-1.4088682	-3.1962141	0.3871807
	C	-1.7462262	2.4430269	0.4698347
	H	0.4172808	3.5932859	-0.8213883
	H	1.5617648	3.4843509	0.5188487
	H	-0.7277462	4.1287859	1.3672317
	H	-0.2130062	2.5570809	1.9987997
	H	-2.3770032	1.9528139	1.2170367
	H	-2.3524932	3.1691609	-0.0812523
	H	-4.3661762	0.3156189	-1.5878153
	H	-1.8638312	-0.1828771	-1.8799853
	H	1.8607848	1.2799309	0.0756197
	H	-1.2765232	1.8515859	-1.4434893

Table S9 Cartesian coordinates, optimized geometry, and energies of **AInt 3**

AInt 3			
E_{M06}	E_0	H	G
▪-1031.1845338 $^{\Delta}$-1031.4367978	0.333434	0.353298	0.286392
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.851099	-1030.831235	-1030.898142

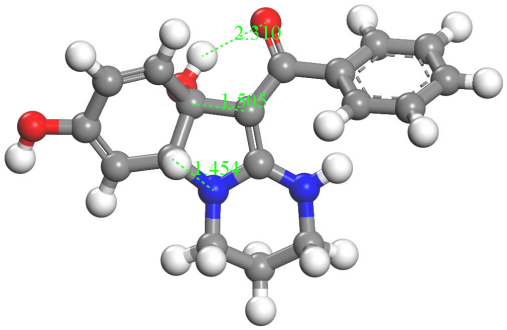


Atoms	x	y	z
O	0.7478855	-2.3079742	1.4037874
C	1.0036475	-1.4357272	0.5656184
C	-0.0909945	-0.6426532	0.0242784
C	2.3978675	-1.1912482	0.1217674
C	-0.0860225	0.6910808	-0.2614406
N	0.8289855	1.6759128	-0.3286536
N	-1.4629185	1.1948708	-0.4681266
C	-3.3594975	-2.5167412	-0.3973476
C	-2.0486445	-2.4239592	-0.1183696
C	-4.3103865	-1.3509662	-0.4566506

	C	-3.7349915	-0.0852042	-0.5038156
	C	-2.2653525	-0.0902642	-0.6581446
	C	-1.5294825	-1.0600542	0.2469394
	O	-1.8402185	-0.8004052	1.6284764
	O	-5.5570535	-1.6229332	-0.4935796
	C	2.6834855	-0.7518232	-1.1770146
	C	4.0031175	-0.5717992	-1.5795476
	C	5.0425725	-0.8173952	-0.6844776
	C	4.7646285	-1.2580642	0.6102664
	C	3.4488115	-1.4557932	1.0085984
	C	0.3870485	3.0434328	-0.0048986
	H	-1.2552495	-1.3871042	2.1390724
	H	1.8722155	-0.5767352	-1.8838686
	H	4.2205605	-0.2446542	-2.5944236
	H	5.5775855	-1.4490982	1.3081764
	H	3.2172175	-1.8068052	2.0128294
	H	6.0746335	-0.6693622	-0.9974696
	H	-3.8171745	-3.4915912	-0.5766576
	C	-0.6843415	2.9836268	1.0767644
	H	-1.4021815	-3.2965542	-0.0259796
	C	-1.8918285	2.1652188	0.6259134
	H	0.0232515	3.5447198	-0.9130796
	H	1.2635185	3.5995788	0.3353234
	H	-1.0100145	3.9947078	1.3437384
	H	-0.2427295	2.5323308	1.9752034
	H	-2.3189035	1.5557678	1.4245054
	H	-2.6791315	2.7764818	0.1760354
	H	-4.3291605	0.7871738	-0.7763076
	H	-1.9417965	-0.3809412	-1.6790006
	H	1.7858405	1.4252368	-0.0953916
	H	-1.4847995	1.7157118	-1.3530506

Table S10 Cartesian coordinates, optimized geometry, and energies of **AInt 4**

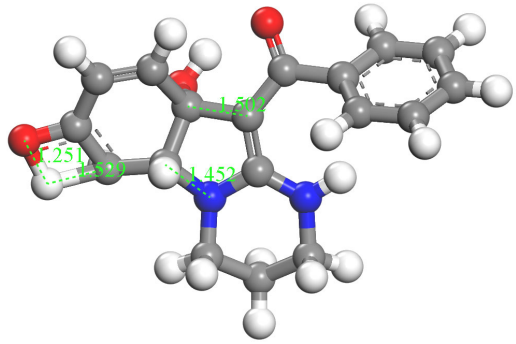
(7,9a-Dihydroxy-1,2,3,4,5a,9a-hexahydropyrimido[1,2-*a*]indol-10-yl)(phenyl)methanone (AInt 4)				
E_{M06}	E_0	H	G	
▪-1031.2423898 $^{\Delta}$-1031.4982461	0.332352	0.352548	0.285123	
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$	
	-1030.910038	-1030.889842	-1030.957267	
	Atoms	x	y	z
	O	-0.7825284	-2.8046250	-0.7566523



C	-1.0284444	-1.6574670	-0.3181643
C	0.0274766	-0.7381850	-0.0646583
C	-2.4513124	-1.2886330	-0.0474993
C	0.0449746	0.6694160	-0.1897853
N	-0.9755504	1.5345540	-0.3209933
N	1.3302556	1.1454110	-0.2400093
C	3.4011436	-2.3004290	0.7070197
C	2.0701786	-2.3285740	0.5083727
C	4.2128236	-1.1516630	0.2943057
C	3.6460396	0.0362340	0.0029617
C	2.1772966	0.0719540	0.2543487
C	1.4585586	-1.1706300	-0.2416533
O	1.7226786	-1.3841100	-1.6471083
O	5.5490466	-1.4201050	0.2641867
C	-2.8179224	-0.6006450	1.1149877
C	-4.1565314	-0.3113970	1.3696267
C	-5.1381394	-0.6981270	0.4588997
C	-4.7803904	-1.3886340	-0.6992423
C	-3.4455704	-1.6921460	-0.9448523
C	-0.8137354	2.9785730	-0.1592733
H	-1.9118124	1.1548460	-0.2360753
H	1.0715146	-2.0570110	-1.9133633
H	-2.0478104	-0.3101350	1.8306107
H	-4.4336064	0.2133710	2.2824377
H	-5.5462394	-1.6944260	-1.4102023
H	-3.1572464	-2.2434650	-1.8389073
H	3.9294946	-3.1417980	1.1550687
H	1.4704236	-3.2008770	0.7637117
H	-6.1840374	-0.4674380	0.6550597
C	0.5654816	3.4030270	-0.6231163
C	1.6221296	2.5414790	0.0425517
H	-0.9626004	3.2535890	0.8971077
H	-1.5962414	3.4731780	-0.7442273
H	0.7298306	4.4579920	-0.3766003
H	0.6438736	3.2978010	-1.7140883
H	2.6202236	2.7719330	-0.3486293
H	1.6417116	2.7126230	1.1345797
H	2.0316126	0.0386140	1.3599787
H	4.2233726	0.9205360	-0.2639303
H	6.0395796	-0.6246120	0.0032177

Table S11 Cartesian coordinates, optimized geometry, and energies of **ATS 4**

ATS 4 (*i* = -2027.92)			
E_{M06}	E_0	H	G
■-1031.159983 Δ-1031.4145719	0.326680 $E_{M06}+E_0$ -1030.833303	0.346581 $E_{M06}+H$ -1030.813402	0.279381 $E_{M06}+G$ -1030.880602

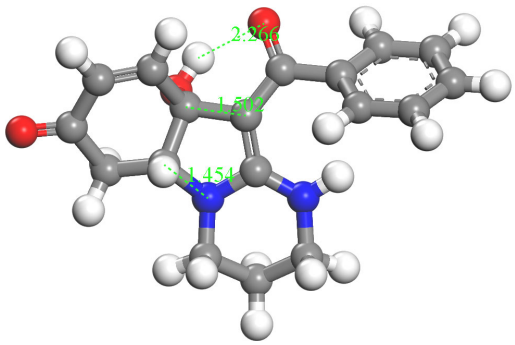


Atoms	*x*	*y*	*z*
O	-0.7810078	-2.7697824	-0.7788623
C	-1.0167058	-1.6316424	-0.3098233
C	0.0519202	-0.7318184	-0.0384563
C	-2.4338328	-1.2547014	-0.0284773
C	0.0909622	0.6811186	-0.1484933
N	-0.9172388	1.5617246	-0.2463583
N	1.3782972	1.1342766	-0.2237633
C	3.3803652	-2.4415654	0.7019057
C	2.0484732	-2.3806044	0.4683827
C	4.1884822	-1.2998074	0.3389587
C	3.6911812	-0.0355624	-0.1243443
C	2.2325112	0.0516806	0.2300827
C	1.4699422	-1.1810574	-0.2472013
O	1.7165122	-1.4207514	-1.6481833
O	5.4679782	-1.2108744	0.5024257
C	-2.7906018	-0.5779244	1.1436307
C	-4.1255758	-0.2776544	1.4043367
C	-5.1127778	-0.6422004	0.4904437
C	-4.7647158	-1.3219194	-0.6770043
C	-3.4338338	-1.6363514	-0.9292593
C	-0.7228398	3.0040106	-0.1031653
H	-1.8594298	1.1992736	-0.1534283
H	1.0145662	-2.0424694	-1.9144633
H	-2.0164308	-0.3068354	1.8625277
H	-4.3955528	0.2380456	2.3243527
H	-5.5351708	-1.6097604	-1.3904173
H	-3.1528018	-2.1787894	-1.8309953
H	3.8510032	-3.3055294	1.1674807
H	1.3975762	-3.2191154	0.7152517
H	-6.1557438	-0.4026704	0.6913907
C	0.6474472	3.3999236	-0.6182483
C	1.7120342	2.5275256	0.0202667
H	-0.8302188	3.2889146	0.9553837
H	-1.5162988	3.5080286	-0.6646793
H	0.8369132	4.4545496	-0.3887873

	H	0.6855502	3.2826706	-1.7101323
	H	2.7013542	2.7203686	-0.4118193
	H	1.7793762	2.7164156	1.1070737
	H	2.1532282	0.0244986	1.3376497
	H	3.9104522	0.1002096	-1.1926383
	H	5.1546492	-0.0138494	0.3174587

Table S12 Cartesian coordinates, optimized geometry, and energies of **AInt 5**

10-Benzoyl-9a-hydroxy-1,3,4,5a,6,9a-hexahydropyrimido[1,2-*a*]indol-7(2*H*)-one (AInt 5)			
E_{M06}	E_0	H	G
▪-1031.2752448 $^{\Delta}$-1031.5254386	0.332713	0.352895	0.284787
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.942532	-1030.922349	-1030.990458

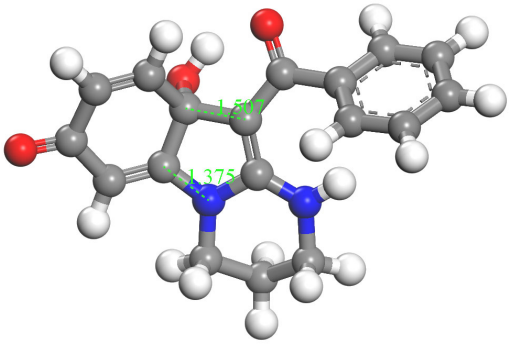


Atoms	*x*	*y*	*z*
O	0.7314430	-2.7872530	0.7840081
C	0.9795550	-1.6539820	0.3116971
C	-0.0790100	-0.7448530	0.0294541
C	2.4014090	-1.2893650	0.0371171
C	-0.1051830	0.6662600	0.1344671
N	0.9099450	1.5385680	0.2315211
N	-1.3904910	1.1308690	0.2099811
C	-3.4034510	-2.3891740	-0.7475849
C	-2.0789220	-2.3588650	-0.5163119
C	-4.3092260	-1.2929580	-0.3449979
C	-3.7014290	-0.0012730	0.1871011
C	-2.2554550	0.0523270	-0.2396329
C	-1.5016650	-1.1845070	0.2258311
O	-1.7683660	-1.4080940	1.6277901
O	-5.5247880	-1.4150740	-0.4422349
C	2.7705900	-0.6258600	-1.1387129
C	4.1094180	-0.3375510	-1.3932759
C	5.0878120	-0.7005410	-0.4693829
C	4.7271820	-1.3668430	0.7020151
C	3.3924620	-1.6697330	0.9481701
C	0.7284840	2.9814390	0.0803131
H	1.8486300	1.1669200	0.1383251
H	-1.1049410	-2.0679920	1.8998311
H	2.0031100	-0.3558300	-1.8651709
H	4.3891950	0.1674960	-2.3162629
H	5.4908220	-1.6533200	1.4232421

	H	3.1015470	-2.2018590	1.8529031
	H	-3.8860020	-3.2443540	-1.2199619
	H	-1.4349600	-3.1950370	-0.7883869
	H	6.1337630	-0.4701790	-0.6654629
	C	-0.6352210	3.3910330	0.6002821
	C	-1.7115540	2.5282110	-0.0317259
	H	0.8331850	3.2594100	-0.9803459
	H	1.5288730	3.4814840	0.6353691
	H	-0.8171190	4.4466580	0.3696941
	H	-0.6697510	3.2757520	1.6924231
	H	-2.6926320	2.7372520	0.4118741
	H	-1.7858500	2.7189610	-1.1176629
	H	-2.2227710	0.0424510	-1.3464819
	H	-3.7886100	-0.0066470	1.2832371
	H	-4.3000290	0.8360510	-0.1930509

Table S13 Cartesian coordinates, optimized geometry, and energies of **3h**

10-Benzoyl-9a-hydroxy-1,3,4,9a-tetrahydropyrimido[1,2-*a*]indol-7(2*H*)-one (3h)			
E_{M06}	E_0	H	G
▪-1030.0675182 $^{\Delta}$-1030.314876	0.309559	0.329315	0.262262
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1029.757959	-1029.738203	-1029.805256



Atoms	*x*	*y*	*z*
O	-0.6980360	-2.7261878	-0.9779243
C	-0.8840850	-1.6198428	-0.4248143
C	0.2192000	-0.7532608	-0.1675373
C	-2.2683450	-1.2338138	-0.0270843
C	0.2770410	0.6475572	-0.1797173
N	-0.6887590	1.5687022	-0.1729703
N	1.5932050	1.0789722	-0.2632793
C	3.4186020	-2.4749408	0.7070337
C	2.1488320	-2.4373588	0.2876017
C	4.3216960	-1.3045458	0.6005117
C	3.7317080	-0.0248668	0.2171827
C	2.4359260	-0.0007518	-0.1479153
C	1.6208280	-1.2344328	-0.4396783
O	1.7923800	-1.5136238	-1.8494873
O	5.5116970	-1.4054938	0.9121427
C	-2.5244720	-0.5997248	1.1944277
C	-3.8308650	-0.2926018	1.5667447
C	-4.8890660	-0.6093138	0.7172767

	C	-4.6411120	-1.2472308	-0.4984523
	C	-3.3384690	-1.5683558	-0.8635433
	C	-0.4362970	3.0046312	-0.0507013
	H	-1.6415100	1.2391102	-0.0565123
	H	4.3255430	0.8730372	0.3798797
	H	1.0632660	-2.1307968	-2.0573983
	H	-1.6961630	-0.3694228	1.8655177
	H	-4.0220880	0.1878862	2.5246957
	H	-5.4681390	-1.4977718	-1.1605423
	H	-3.1352380	-2.0768668	-1.8049833
	H	3.8591890	-3.3719868	1.1404667
	H	1.4988320	-3.3105848	0.3379377
	H	-5.9102010	-0.3647048	1.0049717
	C	0.8945160	3.3527412	-0.6855233
	C	1.9907390	2.4727792	-0.1160993
	H	-0.4455680	3.2898902	1.0124227
	H	-1.2590840	3.5291262	-0.5461653
	H	1.1302990	4.4052912	-0.4952903
	H	0.8374500	3.2130282	-1.7736223
	H	2.9333480	2.6125312	-0.6575733
	H	2.1731990	2.6931982	0.9480007

Table S14 Cartesian coordinates, optimized geometry, and energies of **H_2**

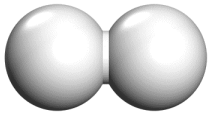
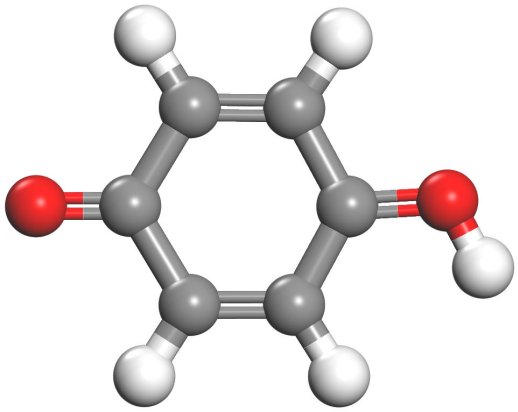
Hydrogen (H_2)				
E_{M06}	E_0	H	G	
▪-1.166775 $^{\Delta}$-1.1709679	0.009955	0.013260	-0.001531	
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$	
	-1.156820	-1.153516	-1.168306	
	Atoms	x	y	z
	H	0.0000000	0.0000000	0.3710960
	H	0.0000000	0.0000000	-0.3710960

Table S15 Cartesian coordinates, optimized geometry, and energies of **B1a′**

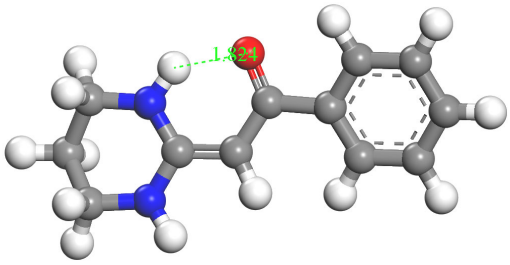
(4-Oxocyclohexa-2,5-dien-1-ylidene)oxonium (B1a′)			
E_{M06}	E_0	H	G
▪-381.5865135 Δ-381.6842757	0.097428 $E_{M06}+E_0$ -381.489085	0.104930 $E_{M06}+H$ -381.481583	0.066532 $E_{M06}+G$ -381.519981



Atoms	*x*	*y*	*z*
C	1.2130835	0.4374435	0.0000000
C	1.2156075	-0.9084825	0.0000000
C	-0.0622655	-1.6755585	0.0000000
C	-1.3336305	-0.9054535	0.0000000
C	-1.3190565	0.4395385	0.0000000
C	-0.0528365	1.1251035	0.0000000
O	-0.1303175	2.4121165	0.0000000
O	-0.0577095	-2.8879265	0.0000000
H	2.1355385	1.0173585	0.0000000
H	2.1325765	-1.4939065	0.0000000
H	-2.2547765	-1.4838985	0.0000000
H	-2.2193665	1.0492845	0.0000000
H	0.7331525	2.8743805	0.0000000

Table S16 Cartesian coordinates, optimized geometry, and energies of **B2g**

1-Phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethan-1-one (B2g)			
E_{M06}	E_0	H	G
▪-650.0104556 Δ-650.1712072	0.242896 $E_{M06}+E_0$ -649.767559	0.256924 $E_{M06}+H$ -649.753532	0.201726 $E_{M06}+G$ -649.808730

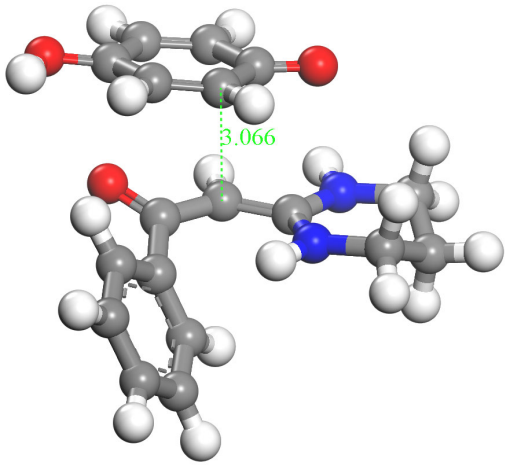


Atoms	*x*	*y*	*z*
N	1.9608605	-1.0129974	-0.0822258
C	3.3733515	-1.3350744	-0.0097568
C	4.2007095	-0.1389564	-0.4411388
C	3.7596725	1.0802966	0.3468982
N	2.3286755	1.2615076	0.1756872
C	1.4555075	0.2246886	0.0550262
C	0.0719695	0.4640576	0.0512212
C	-0.8844835	-0.5721774	-0.0660378
C	-2.3424495	-0.2127754	-0.0459588
C	-3.2640105	-1.2366424	0.1956492
C	-4.6288615	-0.9747294	0.2291012
C	-5.0974505	0.3190356	0.0072402

C	-4.1904085	1.3453806	-0.2480898
C	-2.8241615	1.0815466	-0.2715588
O	-0.5863615	-1.7903554	-0.1675238
H	-0.2449525	1.4955006	0.1824152
H	1.2364595	-1.7374024	-0.1424158
H	3.5624555	-2.1989674	-0.6578288
H	3.6455425	-1.6315304	1.0172822
H	4.0564055	0.0461986	-1.5150128
H	5.2663485	-0.3343754	-0.2718848
H	4.2658075	1.9853966	-0.0085918
H	4.0144185	0.9531586	1.4132272
H	1.9255845	2.1672706	0.3744022
H	-2.8797845	-2.2424344	0.3544452
H	-5.3323195	-1.7829404	0.4254742
H	-6.1664955	0.5266696	0.0276212
H	-4.5488795	2.3568496	-0.4351668
H	-2.1331505	1.8938026	-0.4925008

Table S17 Cartesian coordinates, optimized geometry, and energies of **BCom 1**

BCom 1			
E_{M06}	E_0	H	G
■-1031.634822 $^{\Delta}$-1031.8915984	0.343383 $E_{M06}+E_0$ -1031.291439	0.364894 $E_{M06}+H$ -1031.269928	0.293819 $E_{M06}+G$ -1031.341003

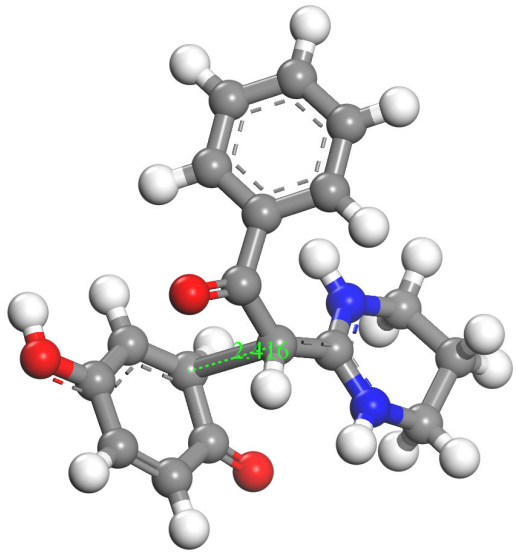


Atoms	*x*	*y*	*z*
N	1.7321817	-2.9279895	-1.2967058
C	1.5062457	-1.6878655	-1.9683958
C	1.8881577	-0.5322365	-1.3756538
C	2.6486067	-0.5305215	-0.1129768
N	2.8882707	-1.8446645	0.5103852
C	2.4659677	-2.9884405	-0.0684808
C	0.0915347	-0.7049155	1.1028462
C	-0.7119793	-1.4161195	0.1577552
C	1.3870917	-4.0789415	-1.8119618
C	0.8464477	-3.9851475	-2.6179808
C	-0.4120153	-2.5996845	-0.1120178
C	2.6271847	-3.9693445	0.3728422
C	1.7169747	0.4374415	-1.8420948
C	0.9923367	-1.6921705	-2.9295288
O	-1.8842003	-0.8057665	-0.5298948
H	-2.8145383	-0.0303665	0.1731032

	H	-2.1221453	-1.1056615	-1.8754338
	H	-3.9491803	0.4561955	-0.4686898
	H	-2.6645513	0.1659395	1.2352492
	H	-3.2431353	-0.6002745	-2.5223338
	H	-1.4249973	-1.7539325	-2.4041718
	H	-4.1580543	0.1819365	-1.8189308
	H	-4.6789763	1.0396185	0.0892122
	H	-3.4149293	-0.8279755	-3.5726618
	H	-5.0445673	0.5654525	-2.3204178
	H	0.2758057	0.6999095	1.2952382
	H	-0.2453983	1.6458975	0.5037202
	H	1.0968197	1.0787965	2.2828882
	H	0.0961567	3.0637635	0.6006092
	C	1.5186707	2.4552295	2.5285502
	C	0.4457617	3.4042745	2.0352712
	C	0.9430267	3.2819865	-0.0678478
	C	2.4739587	2.6315185	2.0127302
	C	0.8052127	4.4368475	2.0986842
	C	-0.7665243	3.6402645	0.2515102
	O	-0.4493393	3.3228065	2.6670862
	O	1.6870967	2.5661305	3.6049062
	H	3.0988977	0.5068295	0.3687242
	H	-0.8864623	1.3477745	-0.2239528
	H	1.5570517	0.3431285	2.8057012
	H	0.6347887	-1.3436385	1.7978082
	H	3.4467447	-1.8460855	1.4453112

Table S18 Cartesian coordinates, optimized geometry, and energies of **BTS 1**

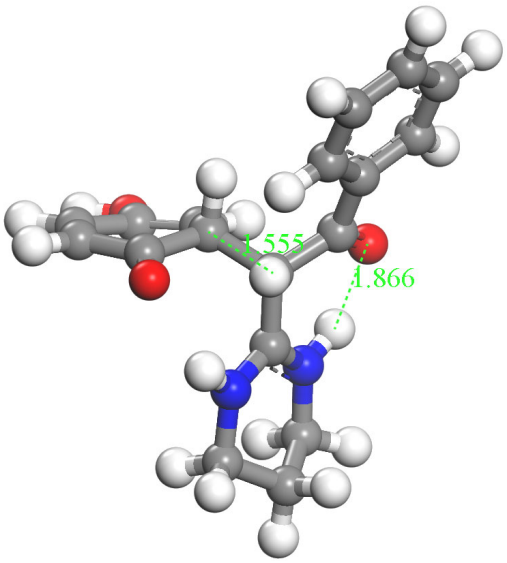
BTS 1 (*i* = -180.36)				
E_{M06}	E_0	H	G	
▪-1031.6327945 $^{\Delta}$-1031.8892048	0.343148	0.364123	0.293881	
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$	
	-1031.289647	-1031.268671	-1031.338913	
	Atoms	x	y	z
	C	1.8338786	-3.2443286	-0.9629976
	C	1.5266786	-2.0131286	-1.5359976
	C	1.8346786	-0.8614286	-0.8356976
	C	2.7514786	-0.9007286	0.3247024
	C	3.0250786	-2.2342286	0.8905024
	C	2.5903786	-3.3447286	0.2665024
	C	0.1326786	-0.6187286	0.8619024



C	-0.8601214	-1.3396286	0.0840024
O	1.5017786	-4.4044286	-1.4893976
H	0.9468786	-4.3029286	-2.2831976
O	-0.7222214	-2.5614286	-0.0341976
H	2.7941786	-4.3450286	0.6430024
H	1.6716786	0.1218714	-1.2747976
H	0.9621786	-1.9714286	-2.4668976
C	-1.9753214	-0.6513286	-0.6256976
C	-2.8089214	0.2645714	0.0277024
C	-2.2444214	-1.0019286	-1.9525976
C	-3.8844214	0.8334714	-0.6461976
H	-2.6336214	0.5099714	1.0759024
C	-3.3022214	-0.4100286	-2.6337976
H	-1.6230214	-1.7518286	-2.4402976
C	-4.1231214	0.5071714	-1.9804976
H	-4.5444214	1.5255714	-0.1268976
H	-3.4980214	-0.6753286	-3.6708976
H	-4.9604214	0.9601714	-2.5079976
C	0.3085786	0.7970714	1.0568024
N	-0.1005214	1.7159714	0.1772024
N	1.0049786	1.1915714	2.1250024
C	0.1299786	3.1553714	0.3188024
C	1.4191786	2.5735714	2.3502024
C	0.3660786	3.5001714	1.7757024
H	0.9968786	3.4403714	-0.2942976
H	2.3976786	2.7345714	1.8732024
H	0.6952786	4.5410714	1.8610024
H	-0.7481214	3.6752714	-0.0784976
H	-0.5686214	3.3984714	2.3443024
H	1.5384786	2.7156714	3.4285024
O	3.2556786	0.1186714	0.7844024
H	-0.6766214	1.3939714	-0.5942976
H	1.3813786	0.4717714	2.7305024
H	0.5764786	-1.2387286	1.6425024
H	3.6319786	-2.2750286	1.7928024

Table S19 Cartesian coordinates, optimized geometry, and energies of **BInt 1**

BInt 1			
E_{M06}	E_0	H	G
■-1031.687453 Δ-1031.9440065	0.345811 $E_{M06}+E_0$ -1031.341642	0.366674 $E_{M06}+H$ -1031.320779	0.295783 $E_{M06}+G$ -1031.391671

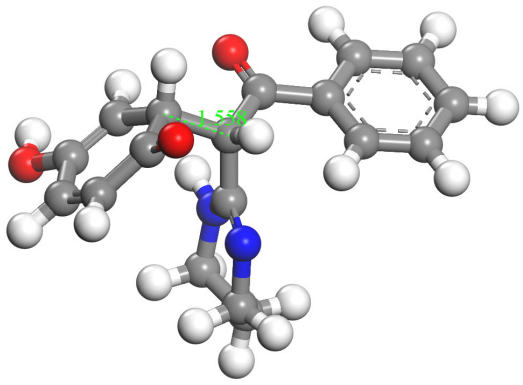


Atoms	*x*	*y*	*z*
C	2.7583646	-1.6876507	-0.8251606
C	3.3462476	-1.9842067	0.4708244
C	2.7187006	-1.7069537	1.6342994
C	1.4363136	-1.0197217	1.6296424
C	0.6736846	-1.0245097	0.3090794
C	1.5047096	-1.2066727	-0.9164386
C	-0.3392734	0.1535563	0.2342874
C	-1.4145024	-0.1964967	-0.7916086
O	3.4787046	-1.9087407	-1.9499786
H	4.3564486	-2.2648167	-1.7477026
O	-1.3147174	0.1925173	-1.9503946
H	1.0561836	-1.0457737	-1.8964416
H	3.1909616	-1.8758897	2.5994574
H	4.3431046	-2.4288197	0.4915354
C	-2.5273164	-1.0673627	-0.3639436
C	-2.7060474	-1.5025597	0.9591174
C	-3.4445384	-1.4704837	-1.3471586
C	-3.7803724	-2.3195197	1.2868224
H	-2.0187904	-1.2144037	1.7537194
C	-4.5172994	-2.2834367	-1.0153006
H	-3.2988124	-1.1314777	-2.3703636
C	-4.6863524	-2.7086737	0.3023514
H	-3.9121804	-2.6516817	2.3142414
H	-5.2249224	-2.5892467	-1.7828486
H	-5.5294764	-3.3452057	0.5639924
C	0.3790106	1.4622283	0.0162754
N	0.4883126	2.0106303	-1.1750546
N	0.9295456	2.0298493	1.0804454
C	1.1749826	3.2826513	-1.4115526
C	1.6641826	3.2964223	1.0209344
C	1.1481276	4.1172063	-0.1455756
H	2.2054976	3.0727203	-1.7287416
H	2.7375006	3.0862073	0.9149034
H	1.7667716	5.0111363	-0.2748076
H	0.6652856	3.7854983	-2.2387886

	H	0.1218396	4.4513133	0.0590334
	H	1.5148546	3.8106853	1.9750414
	O	0.9696106	-0.4800897	2.6286224
	H	0.0532316	-1.9422127	0.4158864
	H	-0.0162104	1.5320973	-1.9257506
	H	-0.7947954	0.2247183	1.2284144
	H	0.8434286	1.5371673	1.9686854

Table S20 Cartesian coordinates, optimized geometry, and energies of **BInt 2**

4-Hydroxy-6-(2-oxo-2-phenyl-1-(1,4,5,6-tetrahydropyrimidin-2-yl)ethyl)cyclohexa-2,4-dien-1-one (BInt 2)			
E_{M06}	E_0	H	G
▪-1031.2477233 $^{\Delta}$-1031.5010141	0.331237 $E_{M06}+E_0$ -1030.916486	0.352139 $E_{M06}+H$ -1030.895585	0.281248 $E_{M06}+G$ -1030.966475

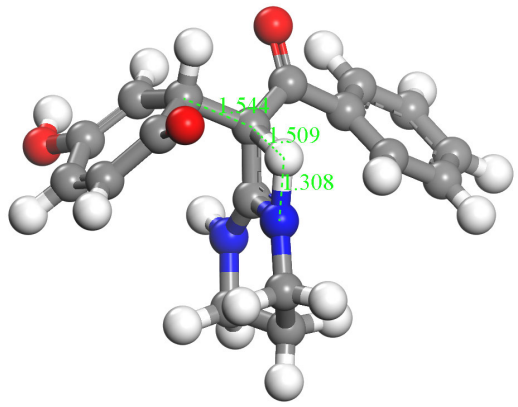


Atoms	*x*	*y*	*z*
C	-3.3025257	-1.1858019	0.8358364
C	-3.9731537	-0.5261309	-0.2722026
C	-3.4714017	-0.5542999	-1.5213966
C	-2.2254277	-1.2659799	-1.8122746
C	-1.3909447	-1.7578209	-0.6317486
C	-2.1043827	-1.7729979	0.6845794
C	-0.0755237	-0.9223769	-0.6441786
C	1.0373263	-1.5617069	0.1757604
O	-4.0178317	-1.1391529	1.9957354
H	-3.5498807	-1.6259639	2.6915514
O	0.7958013	-2.4644529	0.9644394
H	-1.6125107	-2.2803059	1.5152424
H	-3.9809427	-0.0882909	-2.3624766
H	-4.9176047	-0.0288429	-0.0508766
C	2.4254583	-1.0623549	-0.0156126
C	2.7481863	-0.0539309	-0.9333216
C	3.4427793	-1.6397669	0.7556204
C	4.0665683	0.3675881	-1.0711776
H	1.9739903	0.4144111	-1.5394936
C	4.7575153	-1.2194849	0.6138394
H	3.1791763	-2.4242569	1.4624664
C	5.0708523	-0.2136479	-0.3006976
H	4.3095303	1.1515031	-1.7861566
H	5.5426203	-1.6758269	1.2142474
H	6.1021943	0.1171731	-0.4137406

	C	-0.3242177	0.5244181	-0.2526036
	N	-0.3454607	0.7789531	1.0990774
	N	-0.4774767	1.3841901	-1.1910926
	C	-0.8255567	2.0683901	1.5692454
	C	-0.7924147	2.7547781	-0.8118146
	C	-0.3435757	3.1266301	0.5946094
	H	-1.9291787	2.0756441	1.6268554
	H	-1.8835737	2.8934541	-0.9094156
	H	-0.7275717	4.1145431	0.8796294
	H	-0.4359757	2.2411161	2.5799484
	H	0.7554903	3.1738911	0.6338234
	H	-0.3370827	3.4268371	-1.5518726
	O	-1.8418037	-1.4554379	-2.9581676
	H	-1.0855437	-2.7862829	-0.8833736
	H	-0.4830737	-0.0128319	1.7158684
	H	0.2471463	-0.8955729	-1.6946826

Table S21 Cartesian coordinates, optimized geometry, and energies of **BTS 2**

BTS 2 (*i* = -1564.09)			
E_{M06}	E_0	H	G
▪-1031.1748318 $^{\Delta}$-1031.4300657	0.325666	0.346478	0.276467
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.849165	-1030.828354	-1030.898365



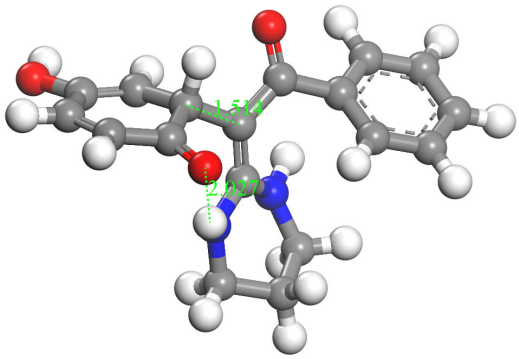
Atoms	*x*	*y*	*z*
C	3.0037235	-1.6467236	-0.9508944
C	3.8263975	-0.5193886	-0.5556884
C	3.6866165	0.0781944	0.6461506
C	2.7091935	-0.4127976	1.6201986
C	1.6773165	-1.4181346	1.1342916
C	2.0138435	-2.0946436	-0.1593994
C	0.2960555	-0.7360666	1.0328526
C	-0.8235355	-1.6645316	0.9763246
O	3.3430505	-2.1620956	-2.1712644
H	2.8103765	-2.9513146	-2.3527844
O	-0.6995245	-2.8562496	1.2824476
H	1.3907805	-2.9429196	-0.4493914
H	4.3265385	0.9017344	0.9590196
H	4.5818055	-0.1859656	-1.2680014
C	-2.1761365	-1.1768896	0.5436766
C	-2.6835085	0.0890014	0.8571446
C	-2.9739595	-2.0629236	-0.1883944

C	-3.9585445	0.4597074	0.4384036
H	-2.0941885	0.7820164	1.4554996
C	-4.2385895	-1.6848436	-0.6252704
H	-2.5838775	-3.0569156	-0.4023254
C	-4.7347655	-0.4205036	-0.3121444
H	-4.3507025	1.4397214	0.7075046
H	-4.8439875	-2.3809666	-1.2040914
H	-5.7292665	-0.1253516	-0.6436994
C	0.2953355	0.5176834	0.2384986
N	0.3374865	0.6899034	-1.0851874
N	0.3050975	1.4857524	1.1251606
C	0.4631535	2.0319324	-1.6498804
C	0.4251145	2.8806664	0.7129736
C	-0.1508785	3.0414144	-0.6898414
H	1.5270275	2.2595214	-1.8248434
H	1.4869415	3.1749654	0.7412066
H	0.0269505	4.0566674	-1.0647594
H	-0.0477605	2.0516024	-2.6189444
H	-1.2397475	2.8876814	-0.6531474
H	-0.1066645	3.5113584	1.4344966
O	2.6996685	-0.0074506	2.7759186
H	1.5619685	-2.1727256	1.9266026
H	0.3945965	-0.1262806	-1.6810644
H	0.2465975	0.4661564	1.9426466

Table S22 Cartesian coordinates, optimized geometry, and energies of **BInt 3**

4-Hydroxy-6-(2-oxo-2-phenyl-1-(tetrahydropyrimidin-2(1*H*)-ylidene)ethyl)cyclohexa-2,4-dien-1-one (BInt 3)

E_{M06}	E_0	H	G
▪-1031.244027 $^{\Delta}$-1031.4989058	0.331786	0.352633	0.282255
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1030.912241	-1030.891394	-1030.961772

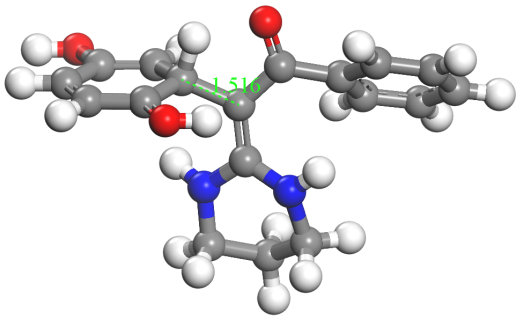


Atoms	*x*	*y*	*z*
C	-4.0441341	-1.1907389	0.7663629
C	-4.7452701	-0.7166769	-0.4061371
C	-4.0913791	-0.3362879	-1.5251591
C	-2.6315741	-0.3051429	-1.5692021
C	-1.9030691	-1.0715309	-0.4882001
C	-2.7075371	-1.3353279	0.7485249
C	-0.4711741	-0.6761219	-0.1942381
C	0.4717889	-1.7570809	-0.2160721

O	-4.8631441	-1.4628619	1.8246559
H	-4.3410011	-1.8167559	2.5603929
O	0.1105169	-2.9472489	-0.2868161
H	-2.1653241	-1.7320969	1.6086899
H	-4.6185191	0.0694791	-2.3867911
H	-5.8322561	-0.6605559	-0.3440741
C	1.9527279	-1.4938499	-0.2444201
C	2.5156859	-0.5210039	-1.0775351
C	2.7958059	-2.3039299	0.5203319
C	3.8961569	-0.3526419	-1.1315941
H	1.8627249	0.0922251	-1.7007841
C	4.1755439	-2.1209519	0.4849379
H	2.3540319	-3.0839469	1.1394069
C	4.7285299	-1.1448139	-0.3416621
H	4.3251019	0.3932801	-1.7997791
H	4.8222499	-2.7497209	1.0954939
H	5.8085189	-1.0098239	-0.3811351
C	-0.1645271	0.6303271	0.2237659
N	0.8508499	0.9103021	1.0797469
N	-0.9373811	1.6915871	-0.1385401
C	1.5887439	2.1726471	1.1186159
C	-0.5638011	3.0312141	0.2927389
C	0.9451789	3.1885281	0.1934539
H	1.5859609	2.5436021	2.1538349
H	-0.8968251	3.1913581	1.3300919
H	1.2668759	4.2007821	0.4667289
H	2.6347629	1.9822201	0.8347669
H	1.2514439	3.0106141	-0.8482431
H	-1.0981621	3.7477841	-0.3382441
O	-2.0378811	0.3028081	-2.4619991
H	-1.8033511	-2.0755639	-0.9645821
H	1.3319319	0.1056001	1.4628079
H	-1.3588191	1.6003171	-1.0601411

Table S23 Cartesian coordinates, optimized geometry, and energies of **BInt 4**

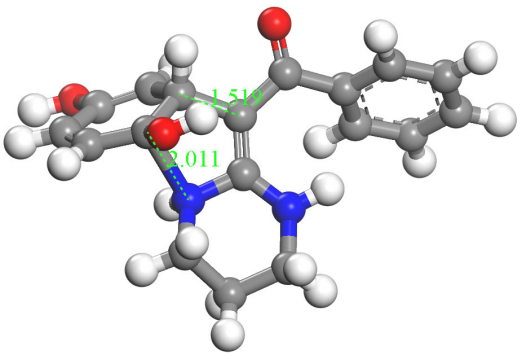
(4-Hydroxy-6-(2-oxo-2-phenyl-1-(tetrahydropyrimidin-2(1*H*)-ylidene)ethyl)cyclohexa-2,4-dien-1-ylidene)oxonium (BInt 4)			
E_{M06}	E_0	H	G
▪-1031.6452328 $^{\Delta}$-1031.9059306	0.342819	0.364204	0.292428
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1031.302414	-1031.281029	-1031.352804



Atoms	*x*	*y*	*z*
C	-3.8224006	-0.9793827	1.1691633
C	-4.5051916	-1.0149507	-0.0835807
C	-3.8507486	-1.1030627	-1.2893807
C	-2.4518006	-1.1587107	-1.2967217
C	-1.6888086	-1.2409847	-0.0511897
C	-2.4614116	-1.0563447	1.1847683
C	-0.2827676	-0.6782337	-0.1223297
C	0.7158914	-1.7101967	-0.0501367
O	-4.4884006	-0.8578347	2.3372653
H	-5.4489146	-0.8474527	2.2103553
O	0.3581804	-2.9040057	-0.1330707
H	-1.9211576	-1.0586997	2.1304533
H	-4.3928036	-1.1002307	-2.2313887
H	-5.5948866	-0.9639997	-0.0855097
C	2.1639204	-1.4263837	0.1603203
C	2.5996034	-0.5198507	1.1349003
C	3.1054974	-2.1541517	-0.5730287
C	3.9594294	-0.3322657	1.3563313
H	1.8709394	0.0239653	1.7376173
C	4.4655504	-1.9471077	-0.3663617
H	2.7584844	-2.8858797	-1.3010007
C	4.8935814	-1.0371117	0.5981523
H	4.2929984	0.3578263	2.1293213
H	5.1933544	-2.5077927	-0.9495797
H	5.9577914	-0.8854097	0.7689383
C	-0.1038666	0.7188883	-0.2928047
N	-1.1349706	1.5654813	-0.0697717
N	1.0308364	1.2597713	-0.7694427
C	-0.9814186	3.0090393	-0.2397867
C	1.4284694	2.6622363	-0.6157857
C	0.4084884	3.4125753	0.2157793
H	-1.1360926	3.2713893	-1.2970647
H	1.5213464	3.1115663	-1.6142107
H	0.5605684	4.4916333	0.1031393
H	-1.7659066	3.5001543	0.3427733
H	0.5246714	3.1686873	1.2818443
H	2.4205894	2.6856583	-0.1452847
H	1.7673354	0.6098483	-1.0209407
O	-1.8290586	-1.1914947	-2.4469597
H	-0.8583966	-1.1648667	-2.2917247
H	-1.3928446	-2.3547837	-0.0481737
H	-1.8856806	1.2324673	0.5241073

Table S24 Cartesian coordinates, optimized geometry, and energies of **BTS 3**

BTS 3 (*i* = -266.42)			
E_{M06}	E_0	H	G
▪-1031.6257363 △-1031.8850954	0.343949 $E_{M06}+E_0$ -1031.281787	0.364292 $E_{M06}+H$ -1031.261444	0.295521 $E_{M06}+G$ -1031.330215

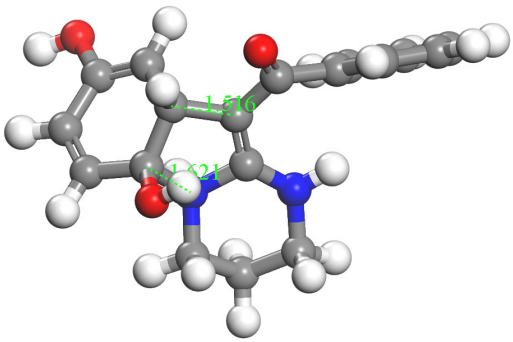


Atoms	*x*	*y*	*z*
C	3.1934394	-1.9730605	-0.9291985
C	4.0962234	-1.1422355	-0.1562535
C	3.6687564	-0.3762755	0.8725515
C	2.2655744	-0.3745075	1.2034625
C	1.3526314	-1.4295515	0.6563175
C	1.9051904	-2.1117335	-0.5532325
C	0.0014524	-0.7827485	0.4019685
C	-1.1849406	-1.5703255	0.7342345
O	3.6509394	-2.6261855	-2.0250845
H	4.6114984	-2.5439215	-2.1165625
O	-1.0624736	-2.5763895	1.4328995
H	1.2441394	-2.7873845	-1.0935605
H	4.3388574	0.2461245	1.4611015
H	5.1557064	-1.1431965	-0.4163355
C	-2.5348956	-1.1693105	0.2501745
C	-2.7497466	-0.7658875	-1.0731075
C	-3.6235316	-1.3009605	1.1190875
C	-4.0393126	-0.4895455	-1.5171265
H	-1.9099186	-0.6994065	-1.7659965
C	-4.9065936	-0.9967795	0.6809185
H	-3.4499196	-1.6489435	2.1361025
C	-5.1155296	-0.5940455	-0.6376595
H	-4.2067046	-0.2021965	-2.5534885
H	-5.7488386	-1.0873085	1.3639735
H	-6.1229066	-0.3715365	-0.9846105
C	0.1061194	0.5441065	0.0464195
N	1.4733974	0.9623565	-0.0734385
N	-0.8424086	1.4796015	-0.1340225
C	1.7549894	2.3832505	0.1832325
C	-0.6191496	2.9257085	-0.2191485
C	0.8035224	3.2378855	-0.6324005
H	1.6257234	2.5543735	1.2619635
H	-0.8319896	3.3761605	0.7629445

	H	1.0068434	4.3022355	-0.4688165
	H	2.8063144	2.5626515	-0.0656105
	H	0.9514774	3.0376945	-1.7034125
	H	-1.3404166	3.3359165	-0.9341325
	H	-1.8006506	1.1787835	0.0225455
	O	1.9765954	0.1682695	2.3762585
	H	1.0486054	-0.0120315	2.6231535
	H	1.2078394	-2.1919365	1.4480785
	H	1.8440924	0.6722835	-0.9841885

Table S25 Cartesian coordinates, optimized geometry, and energies of **BInt 5**

(10-Benzoyl-8-hydroxy-1,3,4,9a-tetrahydropyrimido[1,2-*a*]indol-5a(2*H*)-yl)oxonium (BInt 5)			
E_{M06}	E_0	H	G
▪-1031.6315565 △-1031.8913007	0.345709 $E_{M06}+E_0$ -1031.285848	0.366330 $E_{M06}+H$ -1031.265226	0.296529 $E_{M06}+G$ -1031.335027

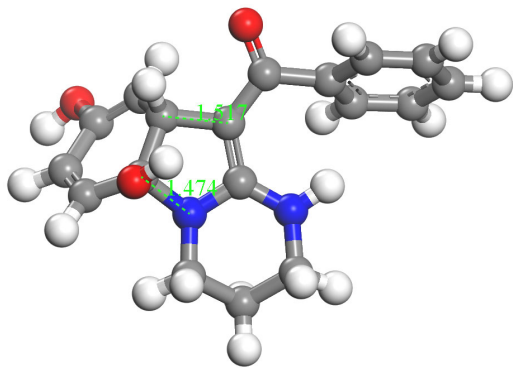


Atoms	*x*	*y*	*z*
C	2.8870989	-2.2242777	-0.8506584
C	3.9195579	-1.3514167	-0.2942964
C	3.6289029	-0.4027667	0.6058266
C	2.2184819	-0.1995107	1.0262286
C	1.2628919	-1.3691037	0.8274036
C	1.6492509	-2.2484377	-0.3267904
C	-0.0734651	-0.6924657	0.5940326
C	-1.3112611	-1.3694987	1.0186916
O	3.2032119	-3.0404207	-1.8860114
H	4.1397579	-2.9699107	-2.1220744
O	-1.2428141	-2.2179677	1.9013446
H	0.9116129	-2.9602877	-0.6948594
H	4.3840969	0.2348433	1.0608786
H	4.9526399	-1.5011667	-0.6102084
C	-2.6111081	-1.0240177	0.3911186
C	-2.7072591	-0.7631907	-0.9816074
C	-3.7705501	-1.0587647	1.1736926
C	-3.9499631	-0.5305847	-1.5623624
H	-1.8109221	-0.7823547	-1.6037084
C	-5.0068171	-0.7997937	0.5957696
H	-3.6864951	-1.2935177	2.2334776
C	-5.0973321	-0.5379507	-0.7715504
H	-4.0252801	-0.3544417	-2.6335854

	H	-5.9058491	-0.8129147	1.2086646
	H	-6.0691971	-0.3511117	-1.2247184
	C	0.0982269	0.5644193	0.1094376
	N	1.5441289	0.8528273	-0.0058094
	N	-0.7311021	1.5350263	-0.3289694
	C	1.9368599	2.2849673	0.1835876
	C	-0.3868981	2.9601243	-0.3211414
	C	1.0656659	3.1475023	-0.7037484
	H	1.7941429	2.5118843	1.2459856
	H	-0.5751811	3.3903423	0.6758646
	H	1.3516869	4.1975833	-0.5773094
	H	3.0037589	2.3586843	-0.0523614
	H	1.2235189	2.8934393	-1.7622524
	H	-1.0508091	3.4602113	-1.0322454
	H	-1.7215381	1.3083493	-0.2764394
	O	2.1751159	0.3706793	2.2671386
	H	1.3197659	0.1938213	2.6978536
	H	1.2226679	-1.9659747	1.7546096
	H	1.8407989	0.5571443	-0.9488974

Table S26 Cartesian coordinates, optimized geometry, and energies of **BInt 6**

(5a,8-Dihydroxy-1,2,3,4,5a,9a-hexahydropyrimido[1,2-*a*]indol-10-yl)(phenyl)methanone (BInt 6)			
E_{M06}	E_0	H	G
▪-1031.2440927 $^{\Delta}$-1031.5017948	0.332348 $E_{M06}+E_0$ -1030.911745	0.352952 $E_{M06}+H$ -1030.891141	0.284085 $E_{M06}+G$ -1030.960007

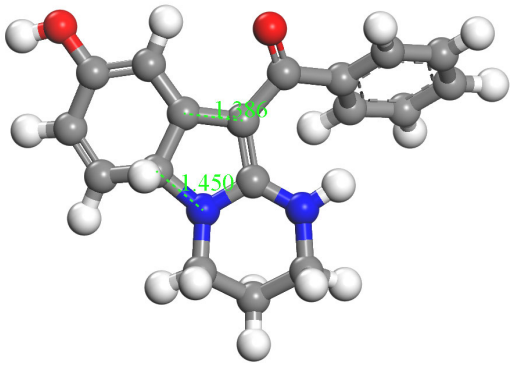


Atoms	*x*	*y*	*z*
C	3.0660921	-2.0994325	-0.8389791
C	4.0112311	-1.0971985	-0.3539461
C	3.6420081	-0.1564255	0.5207769
C	2.2242551	-0.0632145	0.9947289
C	1.3832131	-1.3410075	0.8258849
C	1.8530411	-2.2334665	-0.2874221
C	-0.0048919	-0.7931715	0.5515989
C	-1.1589929	-1.6013565	0.7498739
O	3.4710091	-2.9410785	-1.8407461
H	4.3332091	-2.6648295	-2.1811731
O	-1.0951819	-2.7098635	1.3102159
H	1.1822331	-3.0271025	-0.6140631
H	4.3468921	0.5712455	0.9215039

	H	5.0452271	-1.1486075	-0.7012001
	C	-2.5081239	-1.1396785	0.2780059
	C	-2.7402289	-0.8207035	-1.0633451
	C	-3.5772179	-1.1245415	1.1781589
	C	-4.0207649	-0.4790975	-1.4950941
	H	-1.9132049	-0.8580925	-1.7741181
	C	-4.8505679	-0.7612225	0.7528129
	H	-3.3965779	-1.4081705	2.2144719
	C	-5.0752739	-0.4392925	-0.5856141
	H	-4.1962199	-0.2505105	-2.5455321
	H	-5.6749719	-0.7393475	1.4641019
	H	-6.0748809	-0.1667565	-0.9209411
	C	0.1434741	0.5374865	0.1555119
	N	1.4594631	0.9173815	0.2041759
	N	-0.7777659	1.4405935	-0.2413341
	C	1.8811871	2.3041815	0.1135749
	C	-0.4868879	2.8639715	-0.3483541
	C	0.9432921	3.0534855	-0.8141111
	H	1.8903301	2.7682725	1.1148679
	H	-0.6390259	3.3643725	0.6232479
	H	1.1982871	4.1198955	-0.8223651
	H	2.9099471	2.3253805	-0.2695751
	H	1.0520561	2.6716705	-1.8391481
	H	-1.1967799	3.3007735	-1.0597251
	H	-1.7464129	1.1419175	-0.2348051
	O	2.2901111	0.3554585	2.3456939
	H	1.4102191	0.2376225	2.7412259
	H	1.3971931	-1.9095405	1.7711609

Table S27 Cartesian coordinates, optimized geometry, and energies of **BInt 7**

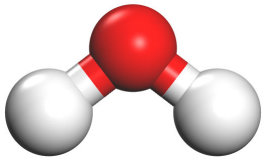
10-Benzoyl-8-hydroxy-2,3,4,9a-tetrahydro-1*H*-pyrimido[1,2-*a*]indol-5-ium (BInt 7)				
E_{M06}	E_0	H	G	
▪-955.2763246 $^{\Delta}$-955.5071197	0.318575	0.337387	0.272303	
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$	
	-954.957750	-954.938938	-955.004021	
	Atoms	x	y	z
	C	-3.5218230	-2.2121895	0.2292472
	C	-4.1650160	-0.9777885	0.6580542
	C	-3.5842870	0.2127215	0.4422442
	C	-2.3512480	0.2449815	-0.3910168
	C	-1.5597060	-1.0233345	-0.3958228



C	-2.2410360	-2.2464095	-0.2712368
C	-0.2120560	-0.7064495	-0.4651738
C	0.8617100	-1.6997625	-0.6538268
O	-4.1599270	-3.3689965	0.3886162
H	-5.0382980	-3.2530565	0.7863102
O	0.6026090	-2.7595095	-1.2106548
H	-1.7448470	-3.1971185	-0.4426858
H	-4.0664300	1.1414965	0.7412872
H	-5.1231630	-1.0452255	1.1723202
C	2.2332360	-1.4208835	-0.1537018
C	2.4519410	-0.7479975	1.0550562
C	3.3231130	-1.9305275	-0.8694958
C	3.7464230	-0.5802005	1.5363002
H	1.6048540	-0.3893095	1.6408652
C	4.6160670	-1.7383005	-0.3998158
H	3.1384210	-2.4759915	-1.7934568
C	4.8280690	-1.0656515	0.8035792
H	3.9112270	-0.0808495	2.4891742
H	5.4621720	-2.1226685	-0.9657978
H	5.8408540	-0.9289135	1.1782102
C	-0.1235160	0.7301425	-0.3798448
N	-1.3455330	1.2717165	-0.1960948
N	0.9475560	1.5022025	-0.5051138
C	-1.5923530	2.7037645	-0.3084058
C	0.8794940	2.9664985	-0.5230428
C	-0.3654580	3.4375265	0.2054792
H	-1.8102330	2.9660035	-1.3564938
H	0.8797200	3.3109355	-1.5668508
H	-0.4895370	4.5157565	0.0601452
H	-2.4748680	2.9528915	0.2922162
H	-0.2590680	3.2590215	1.2841152
H	1.7854150	3.3506875	-0.0438908
H	1.8467590	1.0492485	-0.6377068
H	-2.7312370	0.3555385	-1.4330888

Table S28 Cartesian coordinates, optimized geometry, and energies of **H_2O**

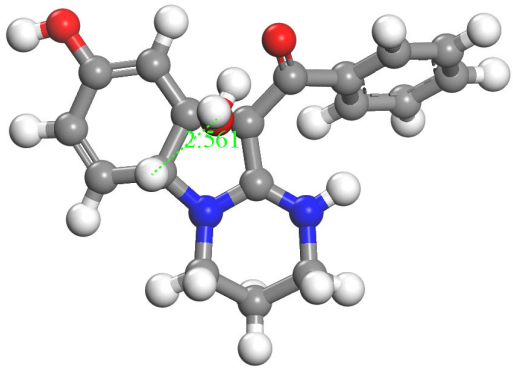
Water (H_2O)			
E_{M06}	E_0	H	G
▪-76.3912345 $^{\Delta}$-76.4248156	0.021392 $E_{M06}+E_0$ -76.369842	0.025171 $E_{M06}+H$ -76.366063	0.003739 $E_{M06}+G$ -76.387496



Atoms	*x*	*y*	*z*
O	0.0000000	0.0000000	0.3909813
H	0.0000000	0.7676190	-0.1954907
H	0.0000000	-0.7676190	-0.1954907

Table S29 Cartesian coordinates, optimized geometry, and energies of **BCom 2**

BCom 2			
E_{M06}	E_0	H	G
▪-1031.6808351 $^{\Delta}$-1031.9438048	0.343102 $E_{M06}+E_0$ -1031.337733	0.365133 $E_{M06}+H$ -1031.315703	0.293047 $E_{M06}+G$ -1031.387788

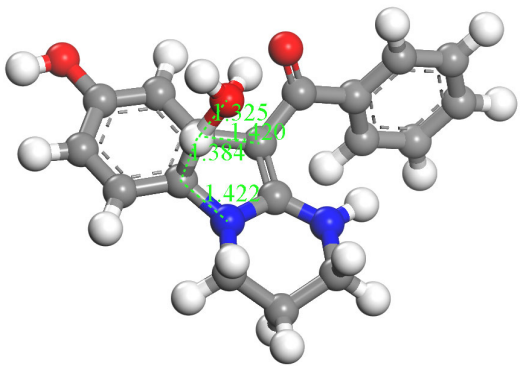


Atoms	*x*	*y*	*z*
C	-3.4096642	-2.1326168	0.5011354
C	-4.0685872	-0.9223228	0.9687784
C	-3.4968882	0.2823202	0.8063404
C	-2.2593422	0.3556632	-0.0105926
C	-1.4609312	-0.9008138	-0.0774356
C	-2.1280142	-2.1341868	0.0035614
C	-0.1212092	-0.5660378	-0.1788566
C	0.9319838	-1.4772138	-0.6597286
O	-4.0350472	-3.3034358	0.6180854
H	-4.9156632	-3.2105858	1.0164334
O	0.6382278	-2.3087638	-1.5184346
H	-1.6264762	-3.0759568	-0.2048646
H	-3.9885342	1.1923572	1.1446204
H	-5.0315222	-1.0184498	1.4693624
C	2.3082448	-1.3655888	-0.1331566
C	2.5591028	-0.8721188	1.1546794
C	3.3732678	-1.8181438	-0.9230886
C	3.8605438	-0.8246288	1.6413944
H	1.7290278	-0.5598708	1.7892244
C	4.6730178	-1.7521278	-0.4409876
H	3.1613728	-2.2152438	-1.9141646
C	4.9166368	-1.2563018	0.8406184
H	4.0512938	-0.4600328	2.6487964
H	5.5011198	-2.0911908	-1.0599276
H	5.9358818	-1.2133128	1.2201504
C	-0.0394852	0.8606792	-0.0179856
N	-1.2599772	1.3834402	0.2185944
N	1.0302818	1.6402642	-0.1183956
C	-1.5163482	2.8169072	0.1580654

	C	0.9517458	3.1035382	-0.0914266
	C	-0.2839192	3.5410132	0.6733724
	H	-1.7542702	3.1101992	-0.8770056
	H	0.9299018	3.4801212	-1.1237846
	H	-0.4172892	4.6226742	0.5662424
	H	-2.3881102	3.0433272	0.7830734
	H	-0.1569622	3.3275302	1.7434304
	H	1.8625828	3.4809162	0.3840544
	H	1.9261148	1.1979862	-0.3005226
	H	-2.6126812	0.4765682	-1.0628766
	O	-1.2349042	-0.5159188	-2.9800386
	H	-1.4246772	-0.6197078	-3.9224146
	H	-0.7098452	-1.3009358	-2.7343256

Table S30 Cartesian coordinates, optimized geometry, and energies of **BTS 4**

BTS 4 (*i* = -1347.50)			
E_{M06}	E_0	H	G
▪-1031.6559004 $^{\Delta}$-1031.9196375	0.338875	0.359685	0.290726
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-1031.317026	-1031.296215	-1031.365174

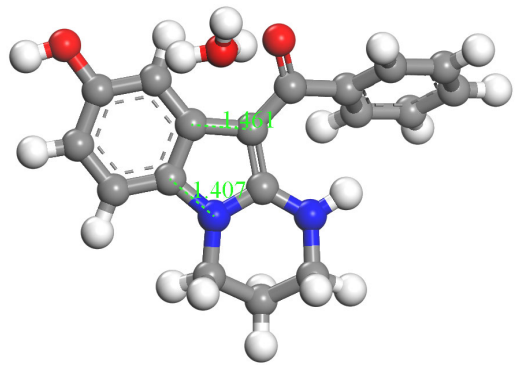


Atoms	*x*	*y*	*z*
C	-3.4350012	-2.1236568	0.4450262
C	-4.2039022	-0.9038398	0.4514972
C	-3.5947672	0.3030082	0.3909402
C	-2.1697222	0.3054792	0.0848342
C	-1.3809452	-0.9181288	0.3001682
C	-2.0533852	-2.1410238	0.3756522
C	-0.0289262	-0.5608688	0.2332472
C	0.9692428	-1.4016658	-0.4633698
O	-4.0590412	-3.3014258	0.5265802
H	-5.0220562	-3.1982338	0.5909962
O	0.5758358	-2.0803658	-1.4160478
H	-1.5246842	-3.0903858	0.4212582
H	-4.1681022	1.2278142	0.4030722
H	-5.2878622	-0.9704708	0.5367812
C	2.3900588	-1.3622748	-0.0836078
C	2.7830118	-0.9211768	1.1864132
C	3.3544118	-1.8058448	-0.9988998
C	4.1291998	-0.9141098	1.5342622
H	2.0273738	-0.6158138	1.9117182
C	4.6969608	-1.7907968	-0.6505918

H	3.0297258	-2.1554678	-1.9769608
C	5.0838598	-1.3442618	0.6141832
H	4.4344818	-0.5851678	2.5254882
H	5.4476718	-2.1302378	-1.3612908
H	6.1376918	-1.3382598	0.8864132
C	0.0145668	0.8737342	0.2496482
N	-1.2376432	1.3831512	0.2850912
N	1.0696438	1.6867702	0.1742512
C	-1.5542312	2.7923672	0.1181862
C	0.9114348	3.1237402	-0.0611708
C	-0.3674932	3.6092292	0.5965582
H	-1.7877372	2.9976082	-0.9390538
H	0.8941878	3.3183072	-1.1435778
H	-0.5287342	4.6664782	0.3611022
H	-2.4471212	3.0209792	0.7134942
H	-0.2774062	3.5221472	1.6878762
H	1.7850598	3.6316822	0.3580722
H	1.9956908	1.2724282	0.1478572
H	-2.2248802	0.1883192	-1.0398908
O	-1.4744382	-0.4013158	-2.4958118
H	-2.0491002	-0.7364358	-3.1974528
H	-0.8529282	-1.1320158	-2.2829438

Table S31 Cartesian coordinates, optimized geometry, and energies of **BInt 8**

BInt 8			
E_{M06}	E_0	H	G
▪-1031.7174991 $^{\Delta}$-1031.9841061	0.344162 $E_{M06}+E_0$ -1031.373337	0.366042 $E_{M06}+H$ -1031.351458	0.295041 $E_{M06}+G$ -1031.422458

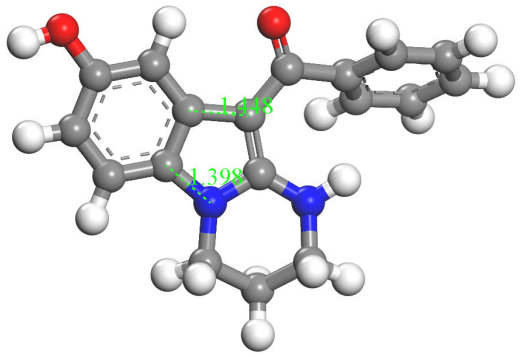


Atoms	x	y	z
C	-3.65200000	-1.43980000	0.21370000
C	-4.25650000	-0.19880000	0.43460000
C	-3.48690000	0.96220000	0.49250000
C	-2.12330000	0.83990000	0.30040000
C	-1.50320000	-0.39130000	0.03930000
C	-2.27250000	-1.55030000	0.01870000
C	-0.06850000	-0.13500000	-0.06130000
C	0.92630000	-1.02890000	-0.42160000
O	-4.36210000	-2.59740000	0.16570000
H	-5.29850000	-2.43170000	0.35110000
O	0.65190000	-2.14780000	-1.06250000

H	-1.84740000	-2.54380000	-0.11480000
H	-3.95930000	1.92430000	0.68140000
H	-5.33530000	-0.13900000	0.57420000
C	2.34920000	-0.86530000	-0.11840000
C	2.76500000	-0.38530000	1.13270000
C	3.30700000	-1.25300000	-1.06700000
C	4.11940000	-0.26840000	1.41700000
H	2.02160000	-0.13900000	1.89050000
C	4.65950000	-1.12080000	-0.78170000
H	2.97910000	-1.64520000	-2.02740000
C	5.06600000	-0.62840000	0.45760000
H	4.44000000	0.08660000	2.39430000
H	5.40050000	-1.40970000	-1.52390000
H	6.12670000	-0.53740000	0.68300000
C	0.08290000	1.28780000	0.15260000
N	-1.13080000	1.83560000	0.35710000
N	1.16820000	2.06180000	0.09080000
C	-1.36780000	3.25850000	0.57280000
C	1.07200000	3.51940000	0.13550000
C	-0.08170000	3.91880000	1.03640000
H	-1.73970000	3.70390000	-0.36160000
H	0.92890000	3.91390000	-0.88210000
H	-0.20470000	5.00700000	1.02650000
H	-2.15380000	3.36040000	1.33090000
H	0.13870000	3.61970000	2.07040000
H	2.02240000	3.90610000	0.51560000
H	2.06530000	1.62460000	-0.08720000
H	-2.01100000	-1.90290000	-2.34940000
O	-1.07310000	-1.94190000	-2.59130000
H	-1.01400000	-2.54850000	-3.34400000
H	-0.43930000	-2.05540000	-1.86780000

Table S32 Cartesian coordinates, optimized geometry, and energies of **3h′**

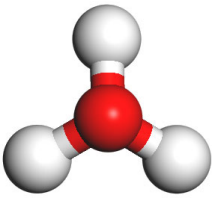
(8-Hydroxy-1,2,3,4,10,10a-hexahydropyrimido[1,2-*a*]indol-10-yl)(phenyl)methanone (3h′)			
E_{M06}	E_0	H	G
■-954.8951288 △-955.1248424	0.305310	0.324269	0.259024
	$E_{M06}+E_0$	$E_{M06}+H$	$E_{M06}+G$
	-954.589818	-954.570859	-954.636105



Atoms	*x*	*y*	*z*
C	-3.8379809	-2.0370896	0.1396533
C	-4.4627829	-0.7845226	0.1724803
C	-3.7035399	0.3850354	0.1131713
C	-2.3282879	0.2539834	0.0241603
C	-1.6864729	-1.0006966	-0.0117487
C	-2.4540889	-2.1629296	0.0448453
C	-0.2620419	-0.7555816	-0.0922467
C	0.7338711	-1.7879086	-0.2271077
O	-4.5623999	-3.1970066	0.1911973
H	-5.5062599	-2.9893416	0.2383023
O	0.4299171	-2.9541976	-0.5006827
H	-1.9946309	-3.1472436	0.0029383
H	-4.1912989	1.3589474	0.1334203
H	-5.5496599	-0.7221966	0.2402803
C	2.1850381	-1.4711886	-0.0155177
C	2.6252861	-0.7731306	1.1130273
C	3.1257741	-1.9786896	-0.9168167
C	3.9869281	-0.5776866	1.3319703
H	1.8966171	-0.3976956	1.8321193
C	4.4841021	-1.7626676	-0.7114197
H	2.7754401	-2.5503456	-1.7751607
C	4.9167971	-1.0639056	0.4154093
H	4.3221701	-0.0497966	2.2235733
H	5.2096441	-2.1511456	-1.4246097
H	5.9812731	-0.9071586	0.5840033
C	-0.1162459	0.6470244	-0.1343977
N	-1.3424639	1.2424044	-0.0484347
N	0.9851861	1.4343684	-0.2524847
C	-1.5925889	2.6698694	-0.1389357
C	0.8386061	2.8305704	-0.6349217
C	-0.3127839	3.4367224	0.1462083
H	-1.9794099	2.9084044	-1.1431117
H	0.6538031	2.9278504	-1.7195537
H	-0.4471989	4.4897444	-0.1275517

	H	-2.3744769	2.9310414	0.5866663
	H	-0.0814619	3.3965574	1.2198953
	H	1.7791421	3.3444574	-0.4095257
	H	1.8564791	0.9651444	-0.4690957

Table S33 Cartesian coordinates, optimized geometry, and energies of **H_3O^+**

Oxonium ion (H_3O^+)				
E_{M06}	E_0	H	G	
▪-76.7254721 $^{\Delta}$-76.7623384	0.034617 $E_{M06}+E_0$ -76.690855	0.038447 $E_{M06}+H$ -76.687025	0.015468 $E_{M06}+G$ -76.710004	
	Atoms	x	y	z
	O	0.0000855	-0.0001733	-0.2293642
	H	0.8812845	-0.3181633	0.0765428
	H	-0.7164635	-0.6035413	0.0764838
	H	-0.1649065	0.9218778	0.0763378